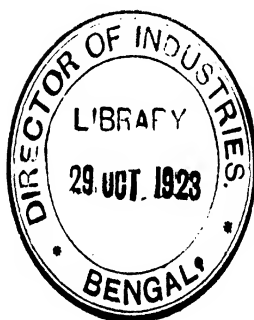


SYNTHETIC RESINS AND THEIR PLASTICS

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Preface.

Vast quantities of resins are needed to meet the world's requirements and the winning of resins from natural sources for various reasons is uncertain. The supply of fossil resins is by no means abundant and reports from some quarters sound an ominous note of approaching exhaustion of the sources of these resins. One need but turn to old formula books to find receipts for making varnishes from amber and other resins now so rare as to be sold only by the ounce. The significance of this observation is that it denotes the passing, from time to time, of raw materials once relatively abundant. Moreover, it marks the entry of synthetic resins into the market and heralds the activity of research chemists who already have demonstrated that it is possible not merely to equal but in many cases to outdo nature by producing synthetically resins having properties greatly desired but not heretofore found in natural products.

To the chemist therefore the users of resins will inevitably turn in the future to provide the means of supplying the prospective deficiency in these necessary substances.

Information on the subject of synthetic products of a resinous character is disseminated through chemical literature but has hitherto been unavailable in any comprehensive form.

This volume has been written with the purpose of placing before the chemist extensive data on a great variety of synthetic products of a resinous character or of an amorphous nature which may lend themselves to substitution in various places where natural resins are now used. The industrial application of synthetic resins, for example, in varnish making and particularly in plastic molding compositions has been considered in detail and the information thus rendered accessible should be of interest to the practical operator.

Presentation of the subject in this manner, it is hoped, will serve as a guide and prove a stimulus to the numerous investigators and practitioners in the field of artificial resins.

The author has devoted many years to the study of the more recent types of synthetic resinous products and the results of his researches are briefly stated herein.

Among the great number of synthetic resins discussed those relating to cumaron and to the condensation products of phenol and formaldehyde necessarily receive prominence owing to the numerous researches which have been made on the preparation and properties of such bodies.

A far more interesting domain to the investigator is that of the

slightly-known resinifying reactions. Some of these only await persistent and systematic investigation to bring fruitful results. In the preparation of this volume a laborious search was made in order to collect extensive data on the little known resins and also substances which have been reported not as resinous but amorphous and which up to the present have been overlooked as possibilities in any commercial sense.

An object also has been to classify in a complete manner all resinifying reactions and if any have been overlooked the author will much appreciate information thereon for inclusion in future editions.

The author avails of this opportunity to express his thanks to Mr. George E. Merkle for assistance in searching the literature and other aid rendered; to Mr. Harry M. Weber, Mr. Trevor S. Huxham, Mr. Joseph R. Kuhn and Mr. Norris Boehmer of the Ellis Laboratories for their interest and cooperation. Mr. Weber's experience with cumaron resin and rosin esters well qualified him to assist in the preparation of Chapters 2, 3, 4 and 16. Mr. Boehmer's experimental work on chlor rubber provided in Chapter 21 information on a commercially little known material. Mr. Huxham devoted many hours to the collection of data relating to molding presses and tests on molded articles discussed in Chapters 24, 25, 26 and 27. The author also wishes to express his appreciation of the courtesies extended by Mr. Charles F. Burroughs and Mr. Walter E. Rahm of the Burroughs Company of Newark, N. J., in connection with the last-mentioned chapters. Prof. Vernon T. Stewart of the Newark Technical School brought to the author's attention several species of resins which otherwise might have been overlooked. Mr. Alexander Murray very kindly revised Chapter 15 on Hardened Rosin and Resinates. Thanks also are due to Dr. L. H. Baekeland, Dr. L. V. Redman, Mr. L. E. Barringer, Mr. A. C. Horn, Mr. W. H. Magoffin, Mr. P. E. Jameson, Dr. Henry A. Gardner, Dr. C. S. Miner, Mr. Walter W. King, Mr. Hylton Swan, Dr. Walther Herzog of Vienna, and others who have furnished data or helpful criticism and to Miss Agnes Davis for very efficient clerical assistance.

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Introduction.

The term synthetic or artificial resin is difficult to define in a concise manner. It properly embraces all resinous products obtained by synthetic or artificial means which are capable of replacing the natural resins. Strictly speaking the term synthetic resins no doubt should apply solely to those resinous products which have been derived primarily from non-resinous raw materials by synthetic means. Products which have been made from natural resins by special chemical treatment such as esterification and the like are, in reality, simply modified resins.

What is a Synthetic Resin?

When synthetic resins are the topic of discussion, and a *definition* of a synthetic resin is requested, answers of a very varied character will be received. Each attempt usually leads to floundering. The simplest definition put forth is that a synthetic resin is a product resembling natural resins and made synthetically. This of course brings up the question of the definition of a natural resin. Chemists commonly regard resins as mixtures of amorphous substances having ill-defined melting points and normally possessing a vitreous lustre or fracture. Yet the natural resins exhibit so wide a range of variation that difficulty arises in fixing their precise limitations. From the many suggestions offered we believe the following, although involved, constitutes the best attempt at a definition:

A synthetic resin is a complex amorphous organic semi-solid or solid material, usually a mixture of substances; built up by chemical reaction and approximating the natural resins in various physical properties; namely, lustre, fracture, comparative brittleness at ordinary temperatures, insolubility in water and fusibility or plasticity when heated or exposed to heat and pressure but commonly deviating widely from natural resins in chemical constitution and behavior with reagents.

Definitions advocated by Abraham¹ for resinous and bituminous materials are as follows:

True Resin.

A term applied to various vegetable principles occurring in, or obtained from, the secretions or saps of certain plants and trees. They are hard, fusible and more or less brittle, non-adherent to slightly adherent solids at ordinary temperatures, usually light colored in mass, having an amorphous structure, conchoidal fracture and "resinous" lustre. They are insoluble in water, but more or less completely soluble in carbon disulphide, benzol, etc. They are oxidation or polymerization products of the terpenes, and generally contain "resin" acids and esters.

¹J. Ind. Eng. Chem. 1913, 11.

Resinous Substance.

A term applied to (a) substances containing true resin; (b) substances of variable origin and composition resembling true resins in their *physical* properties (with the exception of color), and solubility (vide true resins).

Mineral Resin.

A term applied to the solid bitumens (vide bitumen).

Gum Resin.

The semi-solid to solid and usually light colored emulsion or mixtures of true resins with various gums (carbohydrates), constituting the sap of certain plants and trees, partly soluble in water.

Bitumen.

A naturally occurring hydrocarbon complex, often associated with a mineral matrix, insoluble in water, but largely soluble in carbon disulphide, benzol, etc. Its color and hardness are variable.

Pyro Bitumen.

A dark colored, solid, infusible, naturally occurring hydrocarbon complex, often associated with a mineral matrix, insoluble in water, and relatively insoluble in carbon disulphide, benzol, etc.

Bituminous Substance.

A term applied to (a) substances containing bitumens or pyro bitumens; (b) substances resembling either the viscous or solid bitumens, or pyro bitumens in their solubility and physical properties, i.e., having an amorphous structure and dark color in mass.

Maltha.

A dark colored and viscous, naturally occurring hydrocarbon complex, insoluble in water, but completely soluble in carbon disulphide, benzol, etc.

Asphaltum.

A dark colored, and more or less viscous to solid hydrocarbon complex, including: (a) The easily fusible bitumens often associated with a mineral matrix, not having a "waxy" lustre or unctuous feel; (b) fusible residuums obtained from the distillation, oxidation, sulfurization, etc., of bitumens.

Asphaltite.

A dark colored, solid, difficultly fusible, naturally occurring hydrocarbon complex, insoluble in water, but more or less completely soluble in carbon disulphide, benzol, etc.

Tar.

A dark colored, bituminous substance, liquid or semi-liquid at room temperature, often possessing a characteristic "tarry" odor, usually insoluble in water, but miscible with carbon disulphide, benzol, etc., and which on distillation, oxidation, etc., forms a pitch. Its composition and origin are variable.

Pitch.

A dark colored, fusible and more or less viscous to solid bituminous or resinous substance, insoluble in water but more or less completely soluble in carbon disulphide, benzol, etc. Its composition and origin are variable.

Resins by Cracking.

On the other hand artificial resins are not considered to be derived from natural resins by the heat treatment received in the varnish-maker's kettle. Simple "running" or "cracking" of a natural varnish gum although causing deep-seated changes does not transform it into an artificial gum, according to the general understanding.

Classification.

The diminishing supply of natural resins, or *gums* as the trade prefers to call them, has been viewed with apprehension during past years by varnish manufacturers and other large consumers of such products. Developments in synthetic resins have been urged by foresighted consumers of resinous products and in recent years improvements have followed in rapid succession.

Until the commercial advent of the phenol-formaldehyde resins and the cumaron resins the synthetic or artificial resin field had but little material with which to work. The past decade has seen both of these types of resins reach an industrial prominence scarcely contemplated in prior years.

Artificial resins, in the broadest aspect, may be divided into two groups. Group A. Resins made essentially by reacting on non-resinous substances with a resinifying agent. Group B. Resins made by reacting on natural resins with various chemical agents to substantially modify composition and properties.

Group A is the interesting one at present, as from it, resin users expect in future years to supply their manufacturing requirements. This group includes the phenol-formaldehyde products, cumaron resin, glycerine and phthalic acid condensation bodies, ketone resins, the products of polymerization of vinyl compounds, urea and thiourea derivatives and the sulphur phenol resins.

Group B. Various products obtained from natural resins, more especially rosin or colophony, have found a wide-spread use and most of the products are derived by reaction with the resinic acids present in natural resins to obtain metallo-organic compounds or esters. Thus a market is found for numerous resins including the compounds of lime, alumina, zinc, etc., and for resin esters or "ester-gums" as they are called. The latter, in the main, are glycerol combinations with rosin, but harder resins such as congo or other copal species have been used.

Nitrocellulose and pyroxylin varnishes, also cellulose acetate and other cellulose esters are not discussed in the present volume. While these products are extensively used in the lacquer field, they are not properly speaking synthetic *resins*; moreover many treatises on nitro-cellulose are available.²

² See Worden's Nitrocellulose Industry.

Chapter I.

Need for Synthetic Resins and Types Desired.

The waste jar of the laboratory is a morgue for resins wherein few identifications are made. Chemical science has advanced largely because of the study of pure compounds. Purity standards involve crystalline shape and sharp melting points or similar criteria not usually afforded by synthetic bodies of a resinous nature. The reactions giving rise to the formation of resins very often produce a mixture of complex bodies of varying molecular weights, the individuals of which cannot be separated and purified in order to ascertain the chemical constants. Accordingly the formation of a resin during the course of a research may bring dismay to the worker and put an end to progress in a given direction.

Potentialities of Resins.

Chemical literature contains many allusions to reactions which, unfortunately for the goal of the investigator, have yielded resinous bodies. The disgust of the scientific worker over the vicissitudes of research which may have brought him only tars or resins in lieu of anticipated white glistening crystals to some extent is a thing of the past.¹ At least in view of recent developments in the field of synthetic resins it behooves chemists to scrutinize very carefully each and every new resinifying reaction and if consistent with their own endeavors, to fully report reactions of this character in chemical literature in due course. Thus will the field be expanded. The fact that the raw materials involved may be costly should not constitute a deterrent to such scrutiny and publication as subsequent years may bring costly chemicals to much lower price levels. Before the advent of calcium carbide a proposal to make synthetic resins in a commercial way from acetylene would have been the object of ridicule but the discovery of means of manufacturing calcium carbide has made acetylene so much less costly that it is now being employed in the production of such synthetic products. Various other instances of this character could

¹ The disparagement of synthetic resins by scientists dates back over a period of many decades. As early, even, as 1874 we find Edm. ter Meer, Ber. 1874, 7, 1200, stating, in substance:

Investigations aimed to produce compounds of phenol and methylal by direct union, up to the present time have led to no satisfactory results; instead of crystallizable or distillable products, resinous bodies are always formed.

be cited to illustrate the desirability of reporting to the chemical fraternity all reactions which are indicative of resinifying tendencies, instead of considering such occurrences as mishaps and refraining from publication.

Properties Desired.

The question has frequently been asked the author—what is expected of a synthetic resin? Just what properties must the investigator strive to achieve in any synthetic resinous compound on which he is working? Naturally the use to which the resinous substance is to be put will govern the required characteristics. For example, to find a substitute for a fossil resin which is to be used in varnishes one should endeavor to obtain a light colored hard product which will mix readily with drying oils and thinning agents commonly used in varnish manufacture. The varnish maker is particularly bound by the traditions of his craft and probably in no other field will there be found the difficulty existing in the varnish industry of introducing a synthetic resin. This is not due so much to lack of enterprise on the part of the varnish manufacturer as it is to the rather empirical basis on which varnishes are made and in general the secrecy attendant upon the operations of the varnish maker; all of which tend to develop in this trade a resistance to the introduction of anything that is new and different from established customs. Another item which has to be considered is the odor of a synthetic product. Both the varnish maker and the painter and varnisher are so habituated to the odor of natural resins that they resent the "chemical smell" of synthetic products. If a substance does not smell like kauri or shellac or rosin or if it does not have the odor of linseed oil or chinawood oil or if it does not smell like turpentine or varnish makers' naphtha condemnation of the synthetic product on this source alone is not an impossibility and the chemist may never know the reason why his product has not been favorably received. It is therefore desirable in preparing samples for the varnish maker to deodorize by means of steam treatment, air blowing or whatever procedure will serve to minimize or eliminate the objectionable "chemical smell."

Shellac Quality.

On the other hand if the resin is to be put forth as a substitute for shellac, properties of a different nature from that expected in fossil resins will be required. Shellac is a resin of peculiar properties and there is no other natural resin quite like it. While readily soluble in alcohol and therefore capable of use as a quick-drying spirit varnish the dried coating has a quality of hardness and toughness which cannot be found in other resins. As an illustration of this grind a few flakes of orange shellac in a mortar and notice not only how difficult it is to reduce these flakes to a powder but also their elasticity which causes them to fly out of the mortar and make grinding difficult. For that reason as well as on account of hardness it is much easier to grind a

hard copal resin than flake shellac. The copal resin, however, when incorporated with drying oils furnishes a hard, tough varnish relatively resistant to water and severe atmosphere conditions. Shellac, on the other hand, is spotted or stained by water and the lustre of a shellac surface gradually diminishes due to its sensitiveness to moisture. However, owing to the quick-drying qualities of spirit varnish made from shellac and to its hardness shellac is very extensively used for coating purposes. Because of its hardness, sandpaper may be applied to the surface after the solvent has evaporated and the surface thereafter "rubbed down" without gumming of the sandpaper. A synthetic resin to substitute for shellac in this field should be capable of standing the rubbing-down treatment without softening of the surface and gumming of the sandpaper. While the toughness of shellac may not be required in a synthetic resin used in a spirit varnish, at least for cheaper classes of work, that peculiar tough quality of shellac is highly desirable and should be sought for in any synthetic resin aimed completely to replace shellac.²

Shellac Molding.

The hardness and toughness of shellac have caused it to be extensively used in molding various articles which are shaped in hot presses. In this case the shellac is mixed with a filling or extending material, mineral powders usually being employed. The smallest proportion of shellac sufficient to cover and bind together the particles of filler is used. Ordinarily 15 to 20 per cent of shellac suffices with the mineral powders employed, but more bulky fillers may require a larger proportion. In order to remove the hot molded compound from the mold it is necessary first to cool the mold sufficiently to cause the shellac to solidify. Molds employed in making fashioned articles from shellac are usually equipped with means for introducing steam to heat the mold; shaping subsequently taking place under high pressure. Water is then admitted to cool the mold so that the article may be removed without delay. A synthetic resin intended to substitute for shellac in

² Joseph R. Kuhn, connected with the author's laboratory, employs the following preliminary steps to determine the fitness of a synthetic resin in substitution for shellac. 1. Determine whether or not the resin is soluble in alcohol or alcohol and a small percentage of solvent naphtha, say 5 per cent. It is desirable to have the resin completely soluble so as to eliminate any waste of resin. 2. Determine how the resin solution behaves under the brush and whether or not it is free from stringiness. Some resin solutions when applied with a brush string out instead of flowing smoothly. 3. Ascertain whether or not the coating liberates the solvent quickly and whether, when dry, the coating sands well. This is determined by allowing a coating of the solution to dry on wood for about half an hour, then sanding with a piece of fine sandpaper. The sandpaper should slide easily over the coated surface and should not fill or gum up. The surface should be smooth and the wood pores filled. 4. Determine how the sanded coating stands up under oil varnish. Apply a coat of varnish to the sanded surface; then allow to dry for about 24 hours: examine and see whether the varnish has been held on the surface or whether it has been absorbed by the wood through the substitute. An oil varnish will spread much farther if a good shellac substitute is used.

this direction should have the property of flowing readily in the mold and "wetting" or coating the filler adequately and producing a smooth glossy surface. Preferably such a synthetic resin should have a melting point higher than shellac as molded goods made with a shellac binder are liable to become deformed in hot weather or tropical climates. For example, shellac molded articles for amateur wireless apparatus exposed in shop windows to strong sunlight may become hopelessly misshapen after a short period. Therefore a synthetic resin softening at a temperature somewhat above that of shellac is desirable.

Phonograph Records.

The toughness and hardness of shellac likewise lead to its being used as a binder in phonograph records quite early in the history of that industry and up to the present time no other resinous substance has successfully displaced it. Enormous quantities are used in the production of disc records. The manufacturer of a phonograph record expects to produce a disc which can be played from fifty to one hundred times without any substantial abrasion or wear. Also the record composition must be of such a nature that it may be very quickly molded to the proper shape. Synthetic resins which require long heat treatment to bring about a conversion in the mold are not in general looked upon with favor by the phonograph record manufacturer. Most synthetic resins heretofore tried, with the exception of those capable of hardening in the mold, have not the enduring qualities of shellac and after a record has been played a dozen times or so the undulating surface becomes worn and ceases to reproduce a pure tone.

Source of Shellac.

India is the principal country from which shellac is derived and for various reasons shellac experiences very wide fluctuations in price in the market. A synthetic resin having the properties of shellac and being capable of production from raw materials fairly stable in price would be a valuable addition to the list of synthetic products.

Phenol Formaldehyde Resinous Condensation Products.

Shellac has very good electrical insulating qualities and molded articles made from it are generally satisfactory in this respect but the fusibility of shellac makes it undesirable when the insulated material demands the quality of resistance to heat. In such a case resins made by condensing phenol with formaldehyde find extensive use. These well-known synthetic products are fully described in Chapters 6, 7, 8 and 9, and it is not the author's purpose to discuss them here, other than to call attention to certain properties which are peculiar to these resins and which have led to their widespread use. The phenol formaldehyde resins as prepared specifically for molding purposes have the property of setting or hardening in the mold. This is called "curing" by the practical man and is analogous in a way to the curing of

rubber in the vulcanizing process. While hard rubber may require an hour or more for vulcanization the setting of the phenol formaldehyde resins in the case of most small articles requires treatment in the mold for only a few minutes so that the production from any given mold is much greater than that in the molding of rubber and the labor cost in most instances is considerably lower. These heat-set or thermo-rigid phenol formaldehyde resins or resinoids possess very satisfactory electrical insulating qualities. Because of their adequate dielectric strength they have been used quite extensively in the electrical industry.

Water Resistance.

They possess a very marked resistance to water when properly prepared, not being stained or spotted by water and even standing boiling water for a considerable period without great loss of surface finish. Many synthetic resins are lacking in this particular property, that is, adequate resistance to moisture. The quality is highly important in the manufacture of buttons which have to be exposed to boiling water. Furthermore lack of resistance to water indicates the surface gloss or finish which molded articles are usually expected to possess may not be permanent. In the case of the phenol formaldehyde resins the glossy surface finish persists indefinitely. The resistance of synthetic or artificial resins to various agents differs greatly. Some of these, such as the phenol sulphur resins having a high content of combined sulphur (described in Chapter 19), are notably resistant to strong sulphuric acid. Others are resistant to alkali and still others to various organic solvents. Cumaron resins in general show a high degree of resistance to caustic alkalis.

Color.

It may not be amiss at this point to mention the desirability of aiming to secure light colored synthetic resins. In the manufacture of varnishes color is one of the most important considerations. Large quantities of molded goods are made in black or brown shades but a demand exists for lighter colored molded articles and up to the present time no satisfactory product has been obtained which will enable white or light colored molded articles to be made at a low cost. The investigator, therefore, should bear in mind that any discoveries he may make in the synthetic resin field will be enhanced if his product can be made white or light-yellow. Dark brown or black resins have very limited use in the varnish field because of the availability and cheapness of asphaltic substances. On the other hand, a black resin which has the property of "heat-setting" may prove very valuable in the molding field. For example, furfural reacts with phenol in the presence of an acid catalyzer (hydrochloric acid) to form a black resin. If prepared under proper conditions it may be obtained in a fusible form capable of hardening when heated. In this case the property of setting when heated outweighs the disadvantage of the black color.

Adhesion to Molds.

In the manufacture of molded articles certain other requirements must be met. One of these is that the article must not stick to the mold when the latter is opened. The molds are often of very complicated shape and if sticking occurs aside from marring the surface finish of the molded article, there is danger of breakage and loss of time in cleaning the mold for subsequent molding operations.

Staining of Molds.

Staining of the mold also is undesirable because it indicates the composition has an action on the highly polished metal surface. As the lustre of the molded article is obtained by contact with the polished surface, the loss of that polish in the mold means a poorly finished article. Staining cannot be determined in all cases by making a few trials but can be ascertained only under manufacturing conditions involving the use of the mold several hundred times. Stearic acid has been employed as a mold lubricant, a very small percentage being added to the molding composition in order to prevent sticking of the article to the surface of the mold. This acid, especially in its cruder forms, has been found in the course of repeated use of the mold to affect the polished surface of the latter.

Covering the Filler.

In making molded articles a good surface finish is desired and this calls for proper coverage of the filling material. Fine mineral powders are comparatively easy to cover but the case is different with fibrous fillers such as asbestos and wood flour. In the latter case impregnation by means of a solution of the resin, drying and working the material on differential hot rolls to force the resinous binder thoroughly into the fibrous material, is desirable. A product is obtained in sheeted form which may be used as such or may be ground to a powder. The cost of power for these operations is an item of importance.

Uniformity of Product.

Irrespective of the process by which the synthetic resin is made it will be found to vary in quality from day to day and a molding composition of uniform quality is best obtained by mixing several batches. In this way the slight variations in manufacture which may considerably affect the time of molding, surface finish and other properties are averaged in such a manner that a substantial degree of uniformity is secured.

Rosin.

On account of its lack of resistance to water, rosin was once a despised member of the natural resin group. Varnishes containing any substantial quantity of rosin would turn white when the varnish coating became wet. Therefore rosin was used in varnishes in a limited way and the varnish manufacturer always felt somewhat apologetic when explaining the presence of this cheap material. The explanation usually offered was that some rosin was needed to flux fossil resins or hard gums and that only a small amount of rosin was used for the purpose. The Liebermann-Storch reaction is so reliable a test for ascertaining even small quantities of rosin that the user could generally ascertain the presence of this adulteration. There existed however no very satis-

factory quantitative method of determining rosin and large quantities were used in some varnishes to their detriment. Sometimes the varnish product was all too generously fluxed by rosin. Thus rosin acquired an undesirable but well-deserved reputation.

Tung Oil.

About twenty years ago the virtues of Chinese wood oil in varnishes began to be more generally known. This drying oil possessed an unusual resistance to water, having a so-called waterproofing effect when added to varnish. With the hard resins, however, this oil did not give very satisfactory results. The character of the surface on drying was always a matter of doubt. Sometimes the coating would dry clear and brilliant, at other times it would be dull or frosted. The fossil resins were found to be not entirely compatible with Chinese wood oil but, on the other hand, rosin was found to have exceptional merit. It would permit properly prepared Chinese wood oil varnishes to dry without danger of frosting and the wood oil also waterproofed the rosin so that the composition became resistant to water to a remarkable extent. As is well known this oil gelatinizes when strongly heated and if solidification occurs in the varnish kettle the batch is usually ruined. Heating wood oil above its gelatinizing temperature minimizes frosting. Hot rosin has been found an excellent solvent for the gelatinized oil. Thus the wood oil and rosin are mutually beneficial.

Ester Gums.

The next step in the development of rosin varnishes was the reduction in the acidity of the rosin by treatment with glycerine to form the ester or what is known in the varnish trade as "ester gum." The rosin ester was likewise compatible with Chinese wood oil and varnishes made largely from these raw materials proved to be so water-resistant and serviceable that they have come into wide use. Today some of the best known water-resisting varnishes are made from ester gum and wood oil.

Spar Varnish.

Thus a notable change has occurred in the past twenty years in connection with the manufacture of rosin varnishes due to chemical endeavor in utilizing the cheapest of resins. Rosin, which years ago had no standing, being merely an adulterant and destroyer of the life of the varnish, is now used in the form of the glyceride ester, and, incorporated with Chinese wood oil, ranks with the hard resins in utility beside being considerably cheaper. Before the advent of this type of coating composition a spar varnish containing rosin was looked upon with suspicion and rightly so. Today specifications for spar varnish are so drawn as practically to constitute a demand for the use of rosin esters. This much at any rate chemical research has accomplished for that craftsman—the varnish maker—whose empirical knowledge and

secretive attitude have been an obstacle in the past to progress along sound scientific paths.

Fortunately the varnish maker is coming to recognize the important function of the chemist in the varnish plant, perhaps because in the contest between science and empiricism science more and more holds the winning hands.

Solubility.

To find favor with the varnish maker a synthetic resin preferably should be quite soluble in the organic solvents employed in the manufacture of varnishes. If spirit varnish is to be made, the resin should dissolve readily in denatured alcohol or wood alcohol. Resins which are soluble only in acetone, ethyl acetate or solvents somewhat out of the ordinary or solvents which have odors differing considerably from those to which the varnisher and painter are accustomed are not so desirable as those which are capable of being used in the routine solvents. Also there is an objection to the addition of benzol or toluol in any large amount to denatured or wood alcohol. A considerable number of resins are soluble only in mixed solvents of this character. In that case solvent naphtha is more acceptable than either benzol or toluol although ordinarily objections are raised when more than 5 or 10 per cent of solvent naphtha is used in denatured alcohol.

Solvents and Their Rate of Evaporation.

The rate of drying of coatings obtained from solutions of phenol formaldehyde resins in volatile solvents varies considerably with the character of the solvent. Wolff^{2a} has studied the effect of solvents to determine the cause of the persistent tackiness of films produced from some synthetic resins and also the cause of solidification or livering of pigment pastes made with varnishes of this character. Even though the resins are hard and of high melting point their solutions in various solvents frequently produce tacky films. Among the observations made by Wolff was that of the benzol-carrying power of different resins when dissolved in solvents such as ethyl and methyl acetates, methyl formate and acetone. The viscosity curves of the solutions in acetone and benzol mixtures suggest that with increasing proportion of benzol to acetone there is a change from molecular to colloidal dispersed systems. Solutions of the resins change their viscosity very sharply at certain critical changes in the concentration of the benzol. When solutions in acetone and benzol are exposed in a thin layer the acetone evaporates more rapidly than the benzol, hence the concentration of the latter increases. The resin is thrown out of solution as a colloidal gel which has great power to retain some of the remaining solvent. This results in the formation of tacky films. To overcome this trouble, Wolff suggests (1) the use of as large a preponderance as

^{2a} *Farben-Zeit.*, 1920, 25, 668; 1922, 27, 2086; 1922, 28, 31; *Chem. Abs.* 1922, 16, 2610; 1920, 2092; *J. S. C. I.* 1920, 342A.

possible of a single solvent in which the resin is highly soluble, or (2) the addition to a mixed solvent of a third component of suitable evaporation rate to slacken the fractional evaporation; or (3) the selection of such combination of solvents that the last to evaporate has the greatest solvent action on the resin. Wolff notes that the degree of dispersion often is influenced by the addition of small quantities of certain solvents and for this reason mixtures of solvents frequently produce better films. The "blooming" of films produced from solutions of certain resins may be due to differences in the dispersion of the resin.

Colloidal Suspensions.

A varnish base when subjected to intensive mechanical disintegration such as that obtained in the Plauson colloid mill serves as a means of making colloidal suspensions which appear like ordinary solutions.

For example 100 parts of benzol are mixed with 5 to 10 parts of acetone-soluble phenol-formaldehyde resin which has previously been treated with small quantities of acetone. Fossil resin in the amount of 1 to 5 per cent also is present. The mixture is disintegrated in the colloid mill. The suspension gradually begins at a peripheral speed of about 300 meters per minute, but is carried out satisfactorily only at a speed of about 1,500 to 2,500 meters per minute. This treatment is continued for 3 hours at a temperature not over 70°C. The result is a homogeneous lacquer which is not a true solution of the base in benzol, but is a suspenoid colloidal dispersion. Varnishes similar to shellac can be obtained from other artificial resins, such as the oxidized pitches, cumaron resins and vinyl polymerization products, or from natural resins, such as copal, asphalt and colophony.²⁰

Resins for Oil Varnishes.

On the other hand, a synthetic resin which is to be employed in the production of an oil varnish should be soluble in turpentine and mineral spirits or a mixture of these vehicles in order to conform to the expectations of the varnish maker. Although benzol and toluol are much more powerful solvents they are not liked on account of the odor. In the case of benzol also there is the objection of too rapid drying preventing the proper flowing out of the composition so that the work exhibits brush marks. In an oil varnish, however, the solvent effect is the resultant of oil, thinners and other components, and a synthetic resin which may not be soluble in a specified thinner may be found to blend satisfactorily in the varnish composition. In the case of the fossil resins strong heating or "running" in the varnish kettle is required to render the resin adequately soluble in oil and thinner. Natural resins in many cases permit of such strong heating without darkening extensively. Synthetic resins, on the other hand, at least in many cases, appear to be much more susceptible to discoloration on heating so that improvement of solubility by the usual heat treatment in the varnish kettle accorded to natural resins is very often unfeasible with synthetic or artificial resins. Cumaron resin is an instance

²⁰ Chem. Met. Eng. 1923, 81; U. S. Pat. 1,436,820, Nov. 28, 1922.

of a product which has given trouble in the past because some grades darken perceptibly when heated to the usual varnish making temperatures.³

Light Colored Oil Varnishes.

The manufacturer of oil varnish is desirous of producing a clear colorless quick-drying varnish. No raw materials are now available which permit him to manufacture such a product. Pyroxylin lacquers and cellulose acetate solutions at the present time are about the only mediums which yield transparent water-white coatings. These cellulose ester solutions have the disadvantage that being only moderately soluble in volatile solvent thinners a large amount of solvent material has to be used in proportion to the total solids. The coating when dry, therefore, is very thin and the surface is covered and built up only very gradually and with consequent use of a proportionately large amount of volatile solvent which of course in most cases is completely lost. Some improvement has been made by the addition of resins and boiled rape or other boiled oil to the cellulose ester solutions, specifically those made from cellulose nitrate. However, the toughness and flexibility of the nitrocellulose film is very greatly impaired by any substantial amount of these extraneous substances as cellulose nitrate is not compatible with the bulk of the oils and resins. Such extending agents have to be used with caution.

In consequence, therefore, no transparent colorless varnish medium is available having a substantial content of total solids, say 30 to 50 per cent, and not containing excessive amounts of thinning agents. Workers in the field of synthetic resins may occupy their time to advantage following paths which promise to lead to the cheap production of an oil-soluble colorless resin.

Another route for the synthetic resin explorer to travel is that of producing a coating having the extraordinary permanency of Japanese lac. Instead of endeavoring to replace the natural resins ordinarily used in making oil varnishes by synthetic products of equal quality and yielding coatings of about the same perishable character, a far more substantial reward awaits the discoverer of a synthetic product as dur-

³ Joseph R. Kuhn, connected with the author's laboratory, employs the following preliminary steps to determine the fitness of a synthetic resin for oil varnishes. 1. Ascertain whether it is soluble in the vegetable drying oils generally used, by heating a quantity of the resin to a temperature varying between 450 and 650° F. (232-343° C.), adding the cold oil slowly or if warm oil is used the addition may be made faster. 2. Determine if metallic dryers can be incorporated. These are generally added to the resin oil mixture while the latter is hot. 3. Determine whether the resin oil mixture can be thinned with the common thinners, turpentine, petroleum naphtha. Twice as much thinner as oil is usually used. The thinners are added while the resin oil mixture is still hot. 4. Determine whether the varnish so made is tough rather than brittle, by pouring a quantity out on glass. Allow the glass to stand upright until the varnish is dry, then scratch with the finger nail or penknife. The scrapings should consist of curls rather than chips.

able as Japanese lac and which could be applied in the liquid condition at ordinary temperature without the use of a volatile solvent. (See under Japanese lac, Chapter 22.)^{3a}

Nature of Resin Formation.

In a general way the derivation of synthetic or artificial resins may be set forth as follows:

- A. From unsaturated compounds by polymerization.
- B. From oxygen-containing, particularly hydroxy, compounds by condensation.
- C. By the combined effect of both condensation and polymerization.
- D. Action of chlorine, nitric acid and other strong reagents.

A typical example of resins produced by polymerization are those derived from cumaron and indene by treatment with sulphuric acid, aluminum chloride or other polymerizing agents.⁴ The polymerization is undoubtedly due to the unsaturated character of these hydrocarbons and a complex of high molecular weight is formed by bridging at the double bonds. Cyclopentadiene and vinyl compounds also offer another illustration of the resin-forming tendencies of unsaturated compounds. Herzog,⁵ in fact, goes so far as to attribute all resinifying reactions to a condition of unsaturation and calls attention to the behavior of methylene ketone, styrol, methyl isoeugenol, isosafrol, dibenzylideneacetone, isoprene and other bodies. Herzog carried out quite an exhaustive series of observations on substituted thioureas which were capable of yielding carbo-di-imides on heating and attributes the resins obtained to the formation in the first instance of the complex

^{3a} To investigators in the field of synthetic resins a number of papers relating directly or indirectly to this field are of interest. For instance the observations made by Schlick, *Farb.-Z.* 1922, 27, 1439, 1511, 1583, 1650, on colloidal conditions in paint and varnish chemistry warrant careful study. The water-absorbing properties of varnishes and paints have been discussed by Morrell, *J. Oil Color Chem. Assoc.* 1921, 4, 130. Walther, *Chem. Tech. Wochschr.* 1921, 5, 379; *Chimie et industrie*, 1922, 7, 964, considers the advantages of alcohol as a varnish solvent in connection with synthetic resins. A review of the various sources of synthetic resins is given by Tschirch, *Seife* 1921, 44, 288; *Chimie & industrie* 1921, 6, 88. Another paper is that of Pomeranz, *Seifensieder Ztg.* 1922, 49, 29, on the industrial significance of artificial resins in comparison with natural resins. Varnish testing, especially hardness, is described by Wolff, *Farben-Ztg.* 1922, 27, 2555, who also considers methods of measurement of the color intensity of varnishes, *Farben-Ztg.* 1921, 27, 415. A short discussion of synthetic insulation materials is furnished by Kennedy, *Elec. Rev.* 1921, 87, 836. Ogawa and Nishiuchi, *Researches of Electrotech. Lab. (Japan)* 107; *Chem. Abs.* 1922, 16, 3518, have investigated the electrical uses of chlornaphthalene. The advantages of cyclohexanol as a solvent for artificial resins are set forth by Schrauth, *German Pat.* 349,905, Jan. 14, 1919, and of tetrahydrotoluene, tetrahydroxylene, di- and tetrahydrobenzene, and cyclopentadiene by Badische Anilin- und Soda-Fabr., *German Pat.* 348,297, Jan. 20, 1920. See also Rauch, *Z. dent. Ol-Fett Ind.* 1922, 42, 700; *Chem. Abs.* 1923, 344.

⁴ Styrene, cinnamic alcohol, cinnamic aldehyde, eugenol, isoeugenol and safrol are very energetically polymerized by 85 per cent sulphuric acid at 0°, the polymers in these cases being hard resins. Brooks and Humphrey, *J. Am. Chem. Soc.* 1918, 825.

⁵ Oester. *Chem. Z.* 1921, 24, 76.

— N : C : N — serving as a resinophore group. Herzog considers aldehydes to be unsaturated compounds and hence classes their well-known resin-building activities with such reactions of resinification as are noted above. Furfural is an example of an unsaturated compound containing the aldehyde group and capable of appearing simultaneously both in a condensing and polymerizing rôle. In the case of the resins obtained from glycerol and phthalic acid it would appear that condensation occupies the stage of reaction in the first instance probably succeeded by polymerization. Some resins, however, for example, those obtained by the treatment of phenol with sulphur chloride, doubtless are formed simply by aggregation of the molecule through successive linkage of additional molecules of phenol to the phenol sulphur complex until the size of the molecule and the number of isomers becomes so great that the mass assumes resinous characteristics. This is neither condensation nor polymerization.

Another resinophore group, discussed in Chapter 12, is the unsaturated ketonic structure



which readily brings about the formation of resins simply by the application of heat. The theory has been advanced that by desmotropic change the resinification of phenols and formaldehyde, or some stage of the reaction, is chargeable to this resinophore. (See Chapter 7.) As yet no experimental evidence supporting the theory is available.

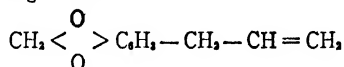
Molecular Complexity of Resins.

At this point it may be noted that the study of resinifying reactions shows in many cases one or more crystalline stages between raw materials and finished product. To obtain a resin it appears necessary to develop a complex of such molecular magnitude that certain colloidal properties characteristic of resins are engendered. Phenol-phthalein becomes a glass-like polymer on heating but may be readily depolymerized to the simple crystalline form by appropriate treatment. On the other hand, viewing a substance of the nature of chlorinated rubber as a resin we may find a change to take place in an opposite way; that is, the highly colloidal and poorly-soluble raw rubber by chlorination becomes depolymerized to a simpler and less colloidal body, brittle rather than elastic and having a notable degree of solubility in various organic solvents. The resinous state is maintained in some cases by the formation of a mixture of isomers or polymers. Ortho and para compounds formed from phenol and formaldehyde give rise to a complex mixture of derivatives which preserve a resinous appearance, whereas the pure compounds doubtless could be obtained in a crystalline form, in some cases. The same observations apply as well to various other resins.

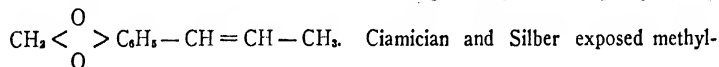
Location of Double Bonds.

The mere condition of unsaturation does not predicate polymerization changes and conversion to resinous substances. On the location of double or triple linkage depends the nature and degree of polymerization phenomena.

Ciamician and Silber* exposed safrol and isosafrol to light. The safrol was unchanged by exposure but the isosafrol was converted to a resin. An examination of the structure of these two compounds will show that in the case of safrol the double linkage is at the end of the side chain



while in the case of isosafrol the double linkage is adjacent the phenyl group



Ciamician and Silber exposed methyl-eugenol and isomethyleugenol to light and found the former to undergo no change while the iso compound was converted into a resin. The same structural differences as regards double linkage obtained with the eugenol compounds as in the case of safrol and isosafrol. In other words, $\text{R}-\text{CH}=\text{CH}-\text{CH}_3$, a di-substituted ethylene, in this case is more readily resinated than the mono-substituted ethylene, $\text{R}-\text{CH}_2-\text{CH}=\text{CH}_2$.

Terminology.

So widespread is the custom of speaking of resins through the materials of their origin that the practice is commonly followed herein. Synthetic resins often are such complex bodies of variable and frequently unknown composition that there is no lack of justification for some laxity in nomenclature at the present time. The progress of chemistry eventually will lead to clarification of resin terminology.

* Ber. 1909, 42, 1389.



FIG. 1.—Miniature Plant for Making Experimental Batches of Synthetic Resins, installed at author's laboratory. The equipment includes digester, drying oven, vacuum dryer, Werner Pfleiderer mixer, grinding mills, and electrically-heated hydraulic press.

Chapter 2.

Cumaron and Indene Resins.*

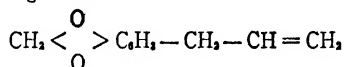
An important source of artificial resins, the so-called cumaron resin is found in certain components of solvent naphtha. In this country technical cumaron resin is usually prepared from a mixture of the hydrocarbon, indene, and cumaron, which contains oxygen. In Europe, cumaron resin is prepared from a mixture of cumaron, indene and their homologues such as methyl cumaron and methyl indene. Both products, however, are known as cumaron resin and have become a staple in the resin market. The resin is obtained by treatment of solvent naphtha, containing these substances, with a polymerizing agent. The first attempts at commercial manufacture resulted in dark sticky products of very limited use. Improved methods and perfected technique now afford a light-colored hard resin of manifold uses. The normal cumaron resin of recent years, a clean, nearly odorless product, should not be confounded with the offensive tars and acid sludges which were obtained in the usual course of refining coal tar naphtha without special means for separation of the resin. Such products although containing cumaron resin had associated with it so many deleterious substances that practically no commercial applications existed.

In this country the fraction of solvent naphtha (heavy benzol, coal tar distillate) boiling between 160-180° C. is the chief source of raw material for the preparation of the resin. In Europe the fraction of naphtha boiling between 150 and 200° C. is principally used; sulphuric acid being the usual polymerizing agent in both cases. Fractions of solvent naphtha boiling above and below the latter range yield resinous and semi-resinous products but up to the present time they are not used to any great extent as the resins obtained have not found sufficient commercial use. There exists the possibility, however, that as our knowledge of the reactions involved and methods of purifying or isolating¹ the raw material increases, other valuable resins will be derived from such sources. In this connection the reader should note

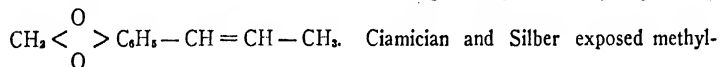
* In connection with the preparation of Chapters 2, 3 and 4, the author wishes to acknowledge the assistance of Mr. Harry M. Weber who has been associated with the author in research work on Cumaron Resin.

¹ Gluud and Breuer (Ges. Abhandlgn. z. Kennt. d. Kohle 1918, 3, 238) have produced cumaron, indene and their homologues by cracking the higher boiling phenols obtained from "low temperature" tar. When solvent naphtha (fraction 155-185° C.) obtained from low temperature coal tar was treated with sulphuric acid a dark brown soft product was obtained which did not resemble cumaron

Ciamician and Silber* exposed safrol and isosafrol to light. The safrol was unchanged by exposure but the isosafrol was converted to a resin. An examination of the structure of these two compounds will show that in the case of safrol the double linkage is at the end of the side chain



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* Ber. 1909, 42, 1389.

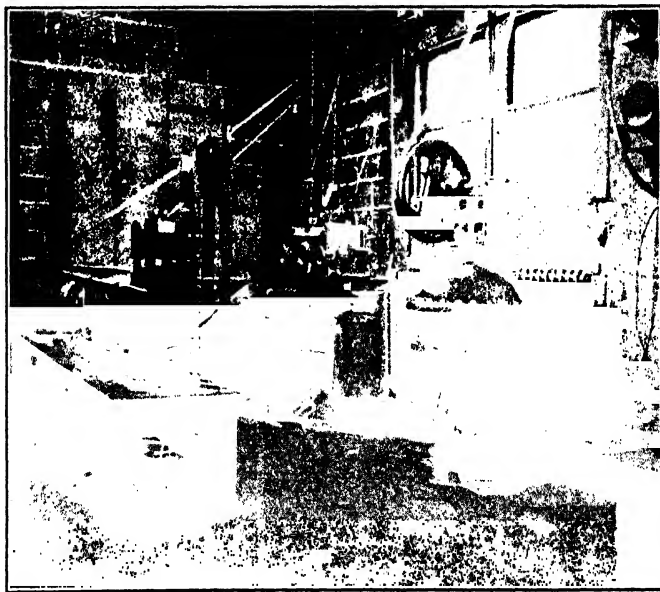
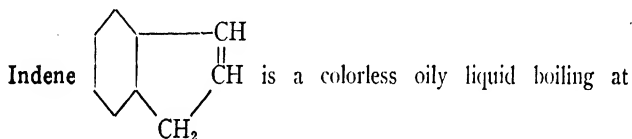


FIG. 1.—Miniature Plant for Making Experimental Batches of Synthetic Resins, installed at author's laboratory. The equipment includes digester, drying oven, vacuum dryer, Werner Pfleiderer mixer, grinding mills, and electrically-heated hydraulic press.

Paracumaron⁶ is a resinous body unaffected by alkalis and most acids; soluble in many of the ordinary organic solvents. It does not dissolve in alcohol. By using an excess of sulphuric acid another polymer of cumaron is produced which is at first soft but finally turns to a brittle infusible mass insoluble in all solvents. By the use of sulphuric acid of 80 per cent strength the soluble polymer is obtained. With acid of increasing strength the insoluble polymer is obtained in progressively greater amounts; the latter exclusively being formed when 95 per cent acid is used. The pure soluble resin possesses a specific gravity of 1.25 and melts at 107-109° C. Its composition represented by the formula C_8H_6O is identical with cumaron but its molecular weight is 4, 8 or 12 times as great. When the resin is heated at 300-350° C. decomposition occurs and a distillate consisting mainly of cumaron together with small quantities of phenol, ethyl phenol, ethyl benzene, benzol, toluol and hydrocumaron is obtained. Kraemer and Spilker⁸ analyzed the insoluble resins obtained from cumaron by the action of strong sulphuric acid and found that combined sulphur was always present. Upon destructive distillation the insoluble resins yielded sulphur, sulphur dioxide, hydrogen sulphide and practically the same products obtained from the soluble resins.



182° C., melting at -2° C. and possessing a specific gravity of 1.002.⁷ It is found in the fractions of coal tar naphtha boiling between 176-182° C.⁸ The hydrocarbon combines with picric acid to form the picrate which decomposes on treatment with steam into indene and picric acid and this reaction is taken advantage of in the preparation of pure indene. It has been prepared by Perkin and Revay,⁹ by distilling a mixture of hydrindene carboxylate and barium formate at atmospheric pressure and also by distilling barium hydrindene carboxylate under reduced pressure (110 mm.).¹⁰ It has also been prepared

⁶ Ordinary cumaron resin of commerce, although a mixture of paracumaron and para indene frequently is called *paracumaron*.

⁷ Ber. 1901, 1887; J. S. C. I. 1901, 557.

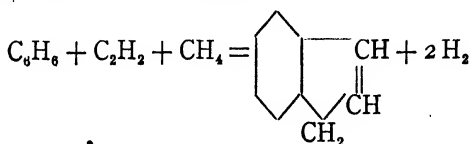
⁸ Spilker and Dombrowsky, Ber. 1909, 573.

⁹ Kraemer and Spilker, Ber. 1891, 3276.

¹⁰ Ber. 1893, 2251; J. S. C. I. 1894, 228.

¹¹ The indene prepared by Perkin and Revay differed in some of its physical but not in its chemical properties from that prepared by Kraemer and Spilker. Gennari (Gazz. Chimie 1895, 468, 474) determined the optical properties of cumaron and indene and found that while the oxygen in the five membered ring in cumaron behaves as the oxygen in furfuran (where the oxygen atom is combined with two carbon atoms) the five membered ring in indene behaves as a homocyclic compound. He suggested, therefore, that the slight difference in the physical properties found by Perkin and Revay were probably due to the presence of cumaron.

by passing acetylene and hydrogen through heated tubes. Meyer¹¹ passed a mixture of equal parts acetylene and hydrogen through two heated tubes (the first being maintained at 640° C. and the second at 800° C.) and obtained indene along with other products, possibly in accordance with the equation



Indene absorbs oxygen rapidly from the air with the formation of cumaron.¹² It also polymerizes on standing at room temperature with the formation of a resinous polymer. The polymerization can be accelerated by boiling under a reflux condenser. Even when indene is distilled at sub-atmospheric pressures polymerization occurs. Kraemer¹³ found that the polymerization of indene takes place with the elimination of hydrogen which simultaneously exerts a reducing action on other indene molecules.¹⁴ Indene may be purified by first treating impure indene with sodamide at 110-115° C. to form soda indene; vacuum distilling the resulting dark oil to remove volatile impurities (the soda indene remaining in the flask) and subsequently decomposing the soda indene with steam. Indene passes over into the distillate. Pure indene is obtained by distilling the product.^{15, 16} Alkyl derivatives of indene can be prepared by treating soda indene with an alkyl chloride. Weissgerber¹⁷ prepared benzyl indene by treating soda indene with benzyl chloride. Sulphuric acid readily polymerizes indene with the formation of para indene.

Para indene is a white resinous body, for which varied molecular weights and melting points have been observed.¹⁸ The polymerization

¹¹ Ber. 1912, 1609.

¹² Weger and Billman, Ber. 1903, 640; J. S. C. I. 1903, 358. Resinous deposits found in illuminating gas distribution pipes and meters are attributed to the polymerization of cumaron and indene or analogous compounds present in the gas.

¹³ Ber. 1903, 645; J. S. C. I. 1903, 358.

¹⁴ Kraemer believes that this may be a general characteristic of all unsaturated compounds and that the change is always preceded by polymerization; the reaction being accelerated by heat. Cumaron resin probably undergoes some such a change and truxene has been isolated from cumaron pitch. The pitch obtained from coal tar is probably formed by the same process, as also the resinification of terpenes, although in the latter case acid resins are formed simultaneously, due to oxidation.

¹⁵ Weissgerber, Ber. 1909, 569.

¹⁶ Spilker and Dombrowsky (Ber. 1909, 573) prepared pure indene from coal tar naphtha boiling between 175-185° C. by Weissgerber's method. The indene obtained by them boiled at 182.2° C.-182.4° C., melted at -2° C. and possessed a specific gravity of 1.002.

¹⁷ Ber. 1911, 1436.

¹⁸ By the action of 75 per cent sulphuric acid on indene Kraemer and Spilker (Ber. 1900, 2257) obtained a white resinous substance having the same composi-

of indene is an exothermic reaction and while the polymerization of cumaron proceeds with but little increase in temperature that of indene produces considerable heat. Aluminum chloride also acts as a polymerizing agent. According to Marcusson¹⁹ three isomers of para indene can be prepared by treating indene in a benzol solution with varied amounts and concentrations of sulphuric acid. With concentrated sulphuric acid the para indene obtained by him melted at 210° C. and was insoluble in ether. By using diluted acid or smaller quantities of concentrated acid a mixture of two para indenenes was obtained, one melting at 165° C., soluble in ether but insoluble in ether-alcohol; and the other melting at 100° C. and soluble in ether-alcohol. Para indene decomposes between 290-340° C.,²⁰ yielding a distillate consisting of indene, hydrindene and phenol.

Methyl Cumaron.

Stoermer²¹ found methyl cumaron in the fraction of coal tar distillate boiling between 185-200° C. It occurs in three isomeric forms; para methyl cumaron boiling at 197-199° C., meta methyl cumaron boiling at 195-196° C. and ortho methyl cumaron boiling at 190-191° C. These are colorless pleasant smelling oils. Stoermer and Boes²² prepared the polymers of methyl cumaron by treating the coal tar fraction boiling between 185 and 195° C. with sulphuric acid. When heated, the polymers decompose into hydrindene and methyl cumarons together with the corresponding cresols.

Dimethyl Cumaron.

Dimethyl cumarons are found in the fraction of tar oils (heavy benzols) boiling between 215 and 225° C.²³ These dimethyl derivatives are reported not to resinify when treated with concentrated sulphuric acid. They impart a methyl violet color to the solution which does not disappear on dilution.

Methyl Indenes.

Boes²⁴ found a mixture of the three isomers of methyl indene in the fraction of solvent naphtha boiling between 200 and 210° C. The isomeric mixture was at first a water-white refractive liquid but soon

tion as indene but of variable melting point and molecular weights which was completely soluble in benzol. Later Kraemer and Spilker (Ber. 1901, 1887) found that the variations in the melting point and molecular weight of para indene obtained by them was due to the presence of cumaron and methyl cumaron in the indene used.

¹⁹ Gläser, Brenn. Chem. 1921, 113.

²⁰ Kraemer and Spilker, Ber. 1900, 2257.

²¹ Ber. 1897, 1700.

²² J. S. C. I. 1900, 1098; Ber. 1900, 33, 3013; J. Chem. Soc. 1901, 80, 31.

²³ Stoermer and Boes, J. S. C. I. 1900, 1098; Ber. 1900, 33, 3013; J. Chem. Soc. 1901, 80, 31.

²⁴ Ber. 1902, 1762.

turned yellow. Concentrated sulphuric acid resinifies (polymerizes) the methyl indenenes. The polymer is sulphur free and of various molecular weights. Hydriodic acid and nitric acid also act on methyl indenenes with the formation of resins. In addition to the resin, nitric acid forms a mixture of acids which Boes identified as hemimellitic and trimellitic acids.

Procedure of Wendriner.

In 1912, Wendriner²² advocated the preparation of cumaron resin by means of successive treatment of solvent naphtha with sulphuric acid of two different strengths. He used naphtha boiling between 160-180° C. and after separation of the tar acids and bases, mixed it with 3 to 5 per cent by volume of 66° B. sulphuric acid. He then added 0.25 per cent by volume of 66° B. continuously in a thin stream, meanwhile agitating the mixture vigorously and allowing the temperature to rise to 110-120° C. The acid was separated and the residual oil neutralized and distilled. He claimed to obtain an improved quality of cumaron resin and a grade of colorless solvent naphtha which did not darken upon exposure to light. He states that if the tar acids and bases are not removed before the polymerization of the cumaron, the resin obtained is not as pure and more 66° B. sulphuric acid (0.5 per cent) must be used.

By allowing the temperature of the naphtha to rise to 110-120° C. Wendriner found²² that secondary reactions took place with the formation of insoluble resins and sulphonated products. By maintaining the temperature at 40-50° C. he not only avoided these reactions which injured the finished product but also was able to carry out the polymerization with the 66° B. sulphuric acid alone. The resin obtained was citron to amber yellow and had a higher melting point. He also points out that overheating during the distillation of the solvent naphtha to recover the resin is to be avoided and direct heating is therefore not used.

Use of Lower Temperatures.

In the course of experiments carried out in the author's laboratory²³ a fraction of solvent naphtha boiling between 160-180° C. was treated with 1 per cent of 66° B. sulphuric acid, with agitation, at room temperature for several hours. The temperature of the mix was below 35° C. throughout the operation. When washed free of acid and steam distilled with superheated steam to remove the naphtha and naphthalene the product was of the consistency of molasses. Upon heating with sulphuric acid (66° Be) to 220° C. for 15 minutes darkening and carbonization occurred without change in hardness. Chlorine combined readily, giving a hard dark substance. Zinc chloride and stannic chloride did not materially affect it and darkening was the only effect observed on exposure to a powerful ultraviolet light.

Other polymerizing agents tried were not as effective as sulphuric acid with the exception of silver oxide. This agent at the boiling point of the naphtha caused the production of a resin which was harder than the resin obtained with sulphuric acid, with the formation of a bright metallic mirror on the walls of the vessel. Iodine, phosphorus trichloride, chromic acid, hydrochloric acid, ammonium dichromate, formaldehyde and potassium hydroxide were without effect. Zinc chloride and anhydrous stannic chloride produced a small quantity of resin.

The soft molasses-like material was distilled under 29" vacuum up to 180° C. with the consequent loss of 57.5 per cent in weight. The product was a resin which became plastic at 38° C, melted completely at 71° C. with a saponification

²² German Pat. 270,993, Aug. 20, 1912; J. S. C. I. 1914, 474.

²³ German Pat. 281,432, Nov. 8, 1913; Chem. Abs. 1915, 2001; J. S. C. I. 1915, 623.

²⁴ J. Ind. Eng. Chem. 1916, 797.

number of less than 0.2 and an iodine number of 38 to 43.5. The distillate was a viscous liquid with an iodine number of 28.5, which is materially lower than that of the finished resin.

An interesting observation upon the unsaponifiable nature of cumaron resin was made. A thin film of cumaron resin on a glass plate withstood the action of a paste of Portland cement without effect but when similar plates were coated with films of drying oils and natural resins the films were quickly attacked and disintegrated.²⁹

Meyer²⁹ prepared a hard pale-colored cumaron resin by polymerizing cumaron and indene with acid in the usual manner and then neutralizing the acid present by vigorously agitating the solution with a slight excess of powdered alkali or alkaline earth carbonates preferably with the addition of small quantities of barium or sodium peroxide. The neutral liquid was separated by decantation, filtration or centrifuging and the volatile constituents removed by distillation.³⁰

Alcohol-soluble Resin.

A form of cumaron resin soluble in alcohol is prepared by Rutgerswerke Akt. Ges.³¹ by polymerizing solvent naphtha (without previous removal of the phenols present) with sulphuric or sulphonic acids. The properties of the resin obtained are modified by the influence of the phenolic bodies.

Polymerization under Pressure.

Cumaron resins were prepared by Sperr and Darrin^{31a} by heating crude solvent naphtha to 100° C.-450° C. under pressures ranging from 50 to 300 lbs. per sq. in. removing the volatile constituents by distillation and finally blowing air or steam through the resinous material obtained. They state that the rate of resinification is increased and the hardness of the resin is improved by the use of copper, silver, gold or platinum as catalysts.³²

Purification by Solvents.

Singer³³ treated the crude resin (obtained by polymerization) with alcohol, acetone, or chlorinated hydrocarbons to remove entrained oils. Coke and sulphuric acid were removed by dissolving the washed resin in an appropriate solvent and separating the solution from these impurities. By subsequent evaporation of the solvent a hard resin was obtained.

²⁹ See U. S. Patents to Ellis No. 999,439; Aug. 1, 1911; 999,708, Aug. 1, 1911, and 1,005,818, Oct. 17, 1911; 1,006,737, Oct. 24, 1911; Ellis and Wells 1,179,413, Apr. 18, 1916; Ellis 1,189,549, July 4, 1916; 1,189,551, July 4, 1916; 1,246,827, Nov. 13, 1917; Brit. Pat. 117,016, Nov. 13, 1917.

³⁰ Ger. Pat. 294,107, Feb. 1, 1916; J. S. C. I. 1916, 1164.

³¹ See also Walpole, Brit. Pat. 145,415, June 16, 1920.

^{31a} Ger. Pat. 302,543, June 9, 1917; J. S. C. I. 1920, 307A.

³² U. S. Pat. 1,263,813, Apr. 23, 1918; 1,296,776, Mar. 11, 1919; Can. Pat. 184,890, June 11, 1918; Brit. Pat. 123,806, Mar. 1, 1918.

³³ They describe the apparatus suitable for carrying out their process in U. S. Pat. 1,314,613; Sept. 2, 1919.

³⁴ Norw. Pat. 29,034, Aug. 26, 1918.

Darrin's Process.

Darrin⁸⁴ produced cumaron resin by treating solvent naphtha (freed of tar acids and bases) with 6.4 per cent of 65° B. sulphuric acid, neutralizing the acid solution with a solution of caustic soda and distilling. He recommended 4 per cent of 50° B. sulphuric acid for the preliminary removal of basic products present in the naphtha. Darrin⁸⁵ describes the neutral resins thus obtained to have a clear reddish color and a melting point as high as 135° C. They may readily be ground without sticking or gumming.

Blended Solvent Naphtha.

In order to obtain cumaron resins which are uniform in character the Barrett Co.⁸⁶ blend solvent naphthas of varied composition so as to obtain a naphtha containing about 30 per cent of polymerizable substances. A light colored resin was obtained by subjecting the blended naphthas, after removal of the tar acids and bases, to a preliminary acid treatment using 0.1 to 0.5 per cent of 60° to 66° B. sulphuric acid. This treatment serves to remove the dark colored constituents which ordinarily would be present in cumaron resin and also to dry the naphtha. After neutralizing and distilling, the naphtha was treated with 1 to 3 per cent of 62° B. sulphuric acid, the acid separated, the oil neutralized with alkali, washed with water and distilled in vacuo to remove the naphtha. A final distillation in vacuo with the introduction of a superheated steam removed the naphthalene and heavy oils present and produced a hard resin. Washing the acid oil was facilitated by using dilute hydrochloric acid as this wash liquor prevented the formation of troublesome emulsions. The hydrochloric acid wash may be substituted for or used after the alkali wash of the oil containing the polymerized resin.⁸⁷

Vacuum Distillation.

Rabinovitz⁸⁸ treated solvent naphtha containing cumaron and indene with sulphuric acid, and after washing and distilling the neutral oil, removed naphthalene and heavy oil from the viscous resinous residue by vacuum distillation up to 200-220° C. and obtained a pale hard resin.

Control of Polymerization.

Capthorne and Tannehill⁸⁹ controlled the degree of polymerization of cumaron resin by diluting the tar acid and base free solvent naphtha boiling between 150 and 200° C. with lighter naphthas (boiling point

⁸⁴ U. S. Pat. 1,297,328, Mar. 18, 1919, J. S. C. I. 1919, 428A; Chem. Abs. 1919, 1647.

⁸⁵ U. S. Pat. 1,326,579, Dec. 30, 1919.

⁸⁶ Brit. Pat. 142,806; April 28, 1920, Chem. Abs. 1920, 2865.

⁸⁷ Brit. Pat. 149,982, 1920; Chem. Abs. 1921, 15, 443. See also Miller and Rhodes, British Pat. 160,148, Sept. 17, 1920; U. S. Pat. 1,365,423, Jan. 11, 1921; Can. Pat. 217,332, Mar. 28, 1922; French Pat. 514,759, 1922; Kunststoffe 1922, 70; Miller, U. S. Pat. 1,360,665, Nov. 30, 1920.

⁸⁸ Can. Pat. 203,100, Aug. 17, 1920; Chem. Abs. 1920, 2994; U. S. Pat. 1,416,062, May 16, 1922.

⁸⁹ U. S. Pat. 1,353,220, Sept. 7, 1920; Chem. Abs. 1920, 3807.

130-150° C.). Later Capthorne⁴⁰ proposed using ammonia gas to arrest polymerization at the desired point.⁴¹

Weak Sulphuric Acid.

According to Demant⁴² the use of weak sulphuric acid in the preparation of polymerized cumaron and indene products is of advantage, in that the sulphuric acid is recoverable without loss. He proposes treating heavy benzols containing cumaron and indene and their homologues with 46-48° B. sulphuric acid and heating the mixture. The polymerized products recovered after separation of the acid and evaporation of the solvent consist of a viscous oil which, by distillation, can be separated into a substance suitable for use as a varnish and an oil. Phosphoric acid may be used as the polymerizing agent as well as sulphuric acid.

Importance of Low Temperatures.

Schneider⁴³ emphasizes the importance of maintaining all solutions at low temperatures during the preparation of cumaron resin. This condition should be maintained not only during the polymerization but also when evaporating the naphtha from the resin. He proposes passing a slow current of air over the naphtha solution containing the polymerized resin to evaporate the naphtha and in this manner to maintain the temperature of the solution below 90° C. He states that this procedure is capable of being carried out with only 2 per cent evaporation loss of the solvent.

Synthetic resins⁴⁴ also are prepared from the homologues of cumaron and indene in the absence of cumaron and indene by treating the naphtha fraction boiling between 190-240° C. with concentrated sulphuric acid. The naphtha is first freed of naphthalene, by freezing and pressing, and then of tar acids by treatment with alkali.

⁴⁰ U. S. Pat. 1,389,791, Sept. 6, 1921.

⁴¹ Wade, Brit. Pat. 166,818, July 15, 1920. Miller, U. S. Pat. 1,395,968, Nov. 1, 1921; Roberts and Rhodes, U. S. Pat. 1,413,558, Apr. 18, 1922, all propose using salt (NaCl) solutions in the washing of the naphtha after polymerization of the cumaron and indene to prevent the formation of troublesome emulsions. Solutions of calcium chloride, ammonium chloride, etc., are also mentioned.

⁴² British Pat. 179,610, Feb. 4, 1921.

⁴³ Ber. Ges. Kohlentechnik 1921, 39; Chem. Zent. 1922, 93, 329; J. S. C. I. 1922, 41, 223A.

⁴⁴ Chem. Met. Eng. 1921, 24, 984, British Pat. 156,668, Mar. 16, 1921.

Darrin's Process.

Darrin⁸⁴ produced cumaron resin by treating solvent naphtha (freed of tar acids and bases) with 6.4 per cent of 65° B. sulphuric acid, neutralizing the acid solution with a solution of caustic soda and distilling. He recommended 4 per cent of 50° B. sulphuric acid for the preliminary removal of basic products present in the naphtha. Darrin⁸⁵ describes the neutral resins thus obtained to have a clear reddish color and a melting point as high as 135° C. They may readily be ground without sticking or gumming.

Blended Solvent Naphtha.

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⁸⁷ Brit. Pat. 149,982, 1920; Chem. Abs. 1921, 15, 443. See also Miller and Rhodes, British Pat. 160,148, Sept. 17, 1920; U. S. Pat. 1,365,423, Jan. 11, 1921; Can. Pat. 217,332, Mar. 28, 1922; French Pat. 514,759, 1922; Kunststoffe 1922, 70; Miller, U. S. Pat. 1,360,665, Nov. 30, 1920.

⁸⁸ Can. Pat. 203,100, Aug. 17, 1920; Chem. Abs. 1920, 2994; U. S. Pat. 1,416,062, May 16, 1922.

⁸⁹ U. S. Pat. 1,353,220, Sept. 7, 1920; Chem. Abs. 1920, 3807.

properties which render its use advantageous. At the present time the production of cumaron is in excess of the demand and this has been true throughout its history in the United States. In Germany, because of the embargo during the War, cumaron was used to replace the natural resins to a great extent,² and there the demand was greater than the production but since this period its use and production have diminished considerably.

Technical Cumaron Resin.

What the trade now recognizes as cumaron resin should not be confounded with the acid sludges obtained in the course of refining of various coal tar distillates. To make a technical cumaron resin requires special skill and apparatus. The production of acid sludge containing some cumaron and indene resin as an incident in refining operations does not represent a method of making a product of a quality ordinarily acceptable to the varnish, enamel, rubber and other industries. The term cumaron resin as now understood designates a technical product of a standard degree of purity. Uses for cumaron resin are constantly growing because of this standardization of quality. To obtain lower grade products likewise of a standard quality some manufacturers prefer to "cut back" a high grade resin by adding softer diluent material.

Grading.

In this country cumaron resin is graded according to its melting point. Commercially the grades of the resin constitute five classes according to their use as follows:

Rubber Grade S	—Melting point	50-65° C.
Medium Soft	—Melting point	65-85° C.
Rubber Grade H	—Melting point	85-100° C.
Medium Hard	—Melting point	100-135° C.
Varnish Grade	—Melting point	135-150° C.

The color of the resin is graded by an arbitrary scale which has reference to the method of grading rosin in this country. For example, No. 1 Grade cumaron resin is about the color of N rosin, while No. 3 Grade cumaron resin is about the color of G rosin. It has been the endeavor in this country to produce the lightest colored resin possible rather than to produce a number of resins of different color grades. As the methods of manufacture are improved resins of a lighter color are being produced until now the resin obtained is comparable with N rosin.³ Small quantities of a still lighter product have been prepared but have been withheld from the consumers until such light material could be produced commercially without a prohibitive cost.

In Germany⁴ cumaron resin is classified into six different grades according to its softening point, as follows:

² Note Fahrion, Chem. Umschau 1922, 29, 103, 111 and 120; Gläser, Brenn. Chem. 1921, 99.

³ The resin is obtained in flake form by spreading in a thin layer on a chilling roll and removing by a scraper. (Miller, U. S. Pat. 1,431,676, Oct. 10, 1922.)

⁴ Gläser, Brenn. Chem. 1921, 113.

Hard and brittle	—Softening above 50° C.
Hard	—Softening between 40 and 50° C.
Medium hard	—Softening between 30 and 40° C.
Soft	—500 or more seconds for nail test
Viscous	—100 to 500 seconds for nail test
Liquid	—Less than 100 sec. for nail test

The last two classes can not really be called resins but are included because of their source of supply. Each of the above classes is sub-divided according to the color of the resin into five different grades, namely, light, light brown, brown, dark brown and black. The standard used for grading the color of the resins is a solution made up of 1.5 grams potassium bichromate in 100 cc. of 50 per cent sulphuric acid solution. Comparison is made against a solution of resin in benzol, using a colorimeter or standard tubes and viewing a cross section of the liquids with the sky as a background. The resin is graded as follows:

Light—When a 10 per cent solution is not darker than the standard.
 Light brown—When a 3½ per cent solution is not darker than the standard.
 Brown—* When light shows through a 10 per cent solution.
 Dark brown—* When light shows through a 5-10 per cent solution.
 Black—* When light does not show through the solution.

Hardness.

Marcusson⁶ found that the hardness of cumaron resin was inversely proportional to the amount of the resin soluble in an ether-alcohol mixture, while the color of the resin was proportional to the percentage of acetone insoluble organic material present. That is, very hard resins contain substances soluble in a mixture of ether and alcohol amounting to 47-48 per cent, hard resins contain 56-58 per cent soluble material, medium hard resins contain 66-68 per cent, soft resins contain 70-85 per cent, while fluid products contain 93-95 per cent of the soluble material.

Solubility.

Bottler⁶ determined the solubility of cumaron resin as follows:

<i>Hard Cumaron</i>		
<i>Solvent</i>	<i>Resin (Bottler)</i>	<i>Color of Solution</i>
Alcohol	Slightly soluble	Light yellow
Absolute alcohol	Easily soluble	Yellow
Carbon tetrachloride	Completely soluble	Yellow to brown
Trichlorethylene	Completely soluble	Yellow
Benzol	Completely soluble	Yellow to red-brown
Turpentine	Soluble (slight residue)	Yellow
Linseed oil	Slightly soluble
<i>Soft Cumaron Resin (Bottler)</i>		
<i>Solvent</i>	<i>Resin</i>	<i>Color of Solution</i>
Ether	Soluble	Yellow
Carbon tetrachloride	Completely soluble	Brownish yellow
Trichlorethylene	Completely soluble	Brown color.
Benzol	Easily soluble	Brownish
Turpentine	Almost completely sol.	Yellowish brown
Ether and 90% alcohol	The resin is pptd.

* Note. The last three grades are determined by viewing the benzol solution of the resin in a tube 15 mm. in diameter. The tubes are placed in a box with suitable apertures and viewed against a 50 candle power light.

⁶ Glaser, Brenn. Chemie 1921, 113. See also review of literature by Ragg, Farben-Z. 1919, 25, 16, 61, 105, 145. Clément and Rivière, Chimie et industrie 1922, 8, 38.

⁶ Kunststoffe, 1915, 5, 277.

Benzol, toluol, solvent naphtha and turpentine are the best solvents for cumaron resin. It is soluble, however, in ethyl acetate, acetone, carbon disulphide, amyl acetate and carbon tetrachloride. It is partly soluble in varnish makers and painters naphtha and gasoline, and entirely so if a small quantity of benzol is added. Most of the vegetable and animal oils are also solvents for cumaron resin. It is soluble in all proportions in rosin oil and pine oil and is softened but not dissolved by petroleum oils. The softer grades of cumaron resin blend with paraffin oil in amounts up to 50 per cent. The harder grades blend in mixtures containing less than 5 per cent or more than 80 per cent of paraffin oil, to give a clear solution. The resin is miscible in all proportions in stearic acid, ozokerite, gilsonite, Japan wax, carnauba wax and beeswax. In ceresin wax, however, cumaron resin is miscible in mixtures of 30 parts or less of ceresin with 70 parts or more of cumaron or 3 parts or less of cumaron resin is miscible with 97 parts or more of ceresin. The solubility of cumaron resin in hard paraffin wax is about the same as that in ceresin. It is not soluble in a low melting or soft paraffin wax.

Cumaron resin is almost insoluble in methyl, ethyl or amyl alcohols, its solubility in these solvents being 2 parts per hundred or less. When prepared according to the process of the Rutgerswerke Akt. Ges.⁷ a resin soluble in alcohol is stated to be obtained.

Solutions of cumaron resin are considerably more viscous than the corresponding solutions of rosin and rosin ester. To obtain solutions of similar viscosity it is necessary to use approximately 1.7 times the amount of solvent necessary for the preparation of a rosin or rosin ester solution.

Paints and Varnishes.

The paint and varnish industry has found the greatest number of uses for and consumes the largest quantity of cumaron resin. Kraemer and Spilker⁸ first suggested the use of cumaron resin as a protective coating for wood and metal applied as a solution of the resin. Since then a number of variations in the solvents employed and the purposes for which the solution is to be used have been suggested. Benzine, gasoline, benzol, turpentine⁹ and solvent naphtha, the latter having its odor masked with benzine¹⁰ have been used. Taking advantage of the unsaponifiable nature of the cumaron resin, its solutions have been used for coating and waterproofing concrete.¹¹ Another purpose for which solutions of cumaron resin have been suggested is as bronzing liquid.¹² The addition of a small quantity of stearic acid to solutions

⁷ German Pat. 302,543, June, 1917. See Chap. 2.

⁸ Ber. 1890, 78.

⁹ Eichler, U. S. Pat. 1,133,432, Mar. 30, 1915.

¹⁰ Krumbhaar, Farben Ztg. 1916, 1086.

¹¹ Ellis, U. S. Pat. 999,439, Aug. 1, 1911; 999,708, Aug. 8, 1911; 1,005,818, Oct. 17, 1911; 1,381,863, June 14, 1922.

¹² Fehrerger, U. S. Pat. 1,157,768, Oct. 26, 1915; Chem. Abs. 1915, 3369.

of cumaron resin which were to be used for this purpose also has been proposed.¹³ A dilute solution of the resin in benzol or toluol, containing oil-soluble dye is recommended for tinting cloth exposed to the weather, such as the lining of automobile tops.¹⁴ Still another purpose for which cumaron resin solution may be used has been proposed by McCoy.¹⁵ By impregnating molded articles made of Portland cement, asbestos, etc. with a solution of cumaron resin and then baking them he renders the articles waterproof and more suitable for use in the manufacture of electrical apparatus. Edison¹⁶ uses a solution of the resin to coat electrodes of electroplating cells to prevent deposition of metal on the coated portions.

Blass¹⁷ prepared a paint by polymerizing the cumaron and indene in solvent naphtha with sulphuric acid and neutralizing the free acid with dry alkalis; using the resulting solution as a paint base. He suggests Portland cement as a suitable pigment. A paint is now prepared¹⁸ by first heating cumaron resin to about 400° F. (204° C.) and maintaining it at this point for a short period of time. The resulting melt is added while hot to a mixture of bitumens and oils and then thinned by means of a suitable solvent. The paint can be used for coating steel and concrete. By this method of procedure "alligation" of the resulting coatings when applied to surfaces which are exposed to the weather has been minimized.

Lacquers, celluloid and celluloid base coatings are said to be improved by the addition of small quantities of cumaron resin.¹⁹ As a substitute for the pyroxylin lacquers Kessler²⁰ proposes employing cumaron resin softened by means of tung oil, using as solvents mixtures of benzol and xylol, monohydric alcohols and fusel oil, or a mixture of all these.

Cumaron resin has promise of becoming extensively used in the preparation of oil varnishes such as floor, spar, or rubbing varnishes. At present a considerable amount of these varnishes are made from it. It is soluble in tung, linseed, soya bean, menhaden, perilla and other drying and non-drying oils. When properly prepared the resulting varnishes are equal and in some cases superior to varnishes prepared from the so-called ester gums and certain of the fossil resins. However, in the preparation of tung oil varnishes it has not the solvent action that rosin has on polymerized tung oil and it is therefore necessary to use a moderate quantity of rosin when preparing "long oil" varnishes of this nature. If lead is used as a drier for varnishes prepared from cumaron resin, it is best to use the lead in the form of the resinate, as

¹³ Shilvock, U. S. Pat. 1,411,673, Apr. 4, 1922; Chem. Abs. 1922, 2035.

¹⁴ Ellis, U. S. Pat. 1,412,014, Apr. 4, 1922.

¹⁵ U. S. Pat. 1,299,847, April 8, 1919.

¹⁶ U. S. Pat. 1,364,359, Jan. 4, 1921; Chem. Abs. 1921, 767.

¹⁷ U. S. Pat. 1,401,034, Dec. 20, 1921.

¹⁸ Private communication.

¹⁹ Lehman and Stocker, German Pat. 281,373, Nov. 26, 1912; U. S. Pat. 1,185,514, May 30, 1916; U. S. Pat. 1,191,801, July 18, 1916.

²⁰ U. S. Pat. 1,411,035, Mar. 28, 1922.

otherwise the lead is precipitated on standing, due to the low acidity of the varnishes produced from cumaron resin.

Spar Varnish.

Long oil or spar varnishes have been prepared with cumaron resin and as an example the following formula is given:

100 lbs. Cumaron resin
20 lbs. Rosin
10 gals. Linseed oil
20 gals. Tung oil
2½ lbs. Cobalt linoleate
40 gals. Thinner

The tung oil and the rosin are heated to 535° F. (280° C.) and then drawn off the fire. When a test sample strings, the linseed oil is introduced to chill the mixture. The cumaron resin is added and the mixture again heated to 510° F. (266° C.) and held at this temperature for 15 to 30 minutes. The batch is then drawn off the fire, cooled, the drier added and the stock thinned by the use of a suitable solvent such as turpentine, naphtha, benzol, etc., or a mixture of these solvents. It will be noted that a comparatively large proportion of linseed oil is used in the above formula but this is of advantage in that a more elastic varnish is obtained. The use of cumaron resin improves the lustre and increases the resistance of the resulting coatings to weathering considerably.

Floor Varnish.

The following is a representative formula for the preparation of medium oil or floor varnishes:

100 lbs. Cumaron resin
15½ gals. Tung oil
2½ gals. Linseed oil
1½ lbs. Cobalt linoleate
34 gals. Thinner

The tung oil is heated to about 470° F. (243° C.) and one-half to three-quarters of the cumaron resin is added while the mixture is still on the fire, with sufficient stirring to prevent the resin from sticking to the bottom and sides of the kettle, as otherwise there would be local superheating of the resin with consequent darkening of the varnish. The temperature of the batch is raised to 535-560° F. (280-293° C.) and the kettle held at this temperature for about 15 to 30 minutes or until a drop on a cold glass plate sets to a fairly hard button. (The mixture, however, should not string.) The remainder of the cumaron resin and all of the linseed oil are added with stirring to check the heat. The mixture is allowed to cool and the thinner and drier added. The resulting varnish is quick-drying, tough, resistant to acids and alkalies and is waterproof.

Varnishes made at temperatures of about 535° F. (280° C.) will sometimes show a slight bloom and it is therefore preferable to prepare the varnish at the higher temperature of 560° F. (293° C.). The resulting varnishes will be slightly darker than those prepared at the lower temperature, but the waterproofing qualities of the varnish offset this slight disadvantage. It is desirable to bear in mind that cumaron resin darkens rapidly at temperatures above 535° F. (280° C.) and it is therefore preferable to "body" the oil as much as possible before the resin is added in order to avoid exposure of the resin to a high temperature for a protracted period. Medium oil varnishes require a thorough cooking of the oil to obtain a waterproof coating. In some cases the "bloom" of a cumaron resin varnish can be corrected by the addition of a small quantity of rosin to the finished varnish; about 5 per cent of the weight of the cumaron resin used being sufficient. The addition of turpentine will sometimes remedy the defect. Coatings made according to the above formula can be rubbed after they have dried 2 or 3 days.

Short Oil Varnish.

For the preparation of short oil or rubbing varnishes the following formula may be used:

100 lbs. Cumaron resin
12 gals. Tung oil
14 oz. Cobalt linoleate
28 gals. Thinner

The procedure and preparation of this type of varnish is similar to that of preparing medium oil varnishes. The kettle is drawn from the fire and held until a sample sets to a hard button. The resulting varnish has a good flow under a brush and can be polished when dry without sweating.

General Considerations.

It should be understood, however, that in the preparation of varnishes the character of the oils, driers and thinners used must be taken into consideration as well as the technique of the varnish maker. The above formulas serve simply as a starting point for the preparation of cumaron resin varnishes and the precise quality or combination of qualities sought may require special study in each case. With slight changes in the proportions of the oils used and variations in the temperature at which the varnish is made satisfactory varnishes for many purposes can be prepared. No doubt those varnish makers who were active in their trade during the period when tung oil first was used in commercial varnish manufacture can recall the discouraging results then obtained due to flatting and "frosting" of the coatings. Those difficulties are largely past history and the varnish manufacturers who were quick to adopt tung oil speedily were rewarded. In a way, the same situation appears in regard to cumaron resin. The varnish makers who soonest acquire the necessary technique in utilizing the resin in varnish production on the large scale should enjoy a commercial opportunity of significance.

Yellowing of Enamels.

In some cases the varnishes prepared from cumaron resin have a tendency to turn yellow on exposure to the weather but for most purposes this is not objectionable. For making white enamels or other light-colored shades, however, this fact should be borne in mind. The tendency of the coatings to become yellow is accentuated by the action of light. An exposure of twenty-four hours to sunlight serves to develop the yellow color to a maximum. The discoloration however is only of minor degree, quite negligible in most applications.

If the varnishes are prepared at lower temperatures than those given in the above formula, namely, below 500° F. (260° C.) it will be noticed that the cumaron resin has a tendency to fall out. On the other hand if the varnishes are heated above 575° F. (302° C.) the resulting varnish will be considerably darker than varnishes properly prepared from the customary natural resins.

Other Compositions Containing Oils.

Sprenger²¹ prepared a varnish by treating oils containing cumaron and indene to which had been added 5 to 10 per cent of animal or vegetable oil, with 21 per cent of concentrated sulphuric acid. During and after the addition of the acid the solution was constantly agitated and care was taken to maintain the temperature below 50° C. for 1 hour. The acid then was allowed to settle and was separated. The acid oil was neutralized with an excess of freshly slaked lime, and the sulphur dioxide formed during the acid treatment of the oils was oxidized with ozone or ozonized air. The calcium sulphate formed was allowed to settle and was separated. The excess of lime unites with the free fatty acids and the varnish oil obtained was of a clear brownish yellow color, which, when applied in a thin film, dried to form a durable elastic coating.

When drying oils, vegetable resins or animal or vegetable waxes are added to a solution of polymerized cumaron and indene before the resins have been removed from the solvent naphtha, upon subsequent evaporation of the naphtha a base is produced suitable for use in varnishes according to Lender and Koch.²² They prepared a base to be used in paints or varnishes by heating tung oil to 220-240° C. and then adding an equal weight of cumaron resin. Eichler²³ recommends the use of linseed, poppy seed, cottonseed or soya bean oils for the preparation of cumaron varnishes. He first heats the resin to about 160° C. and then adds the oil in small portions, cools and adds a suitable thinner. By combining heat-polymerized cumaron resin with oils such as corn oil, soya bean oil, tung oil, etc., Darrin²⁴ obtained a varnish possessing good electrical insulating properties. Later Dayol²⁵ proposed as a vehicle for paints a mixture of 60 per cent of resin, 40 per cent xylol and a small amount of drier and oil of myrbane. A coating composition prepared by Holzapfel²⁶ contains cumaron resin and a small amount of rubber. In some cases stearine pitch also is present.

Linseed Oil Substitutes.

Linseed oil substitutes have been prepared from cumaron and indene. By introducing alkyl or aralkyl groups into indene²⁷ so as to produce monobenzyl indene, xylolated indene or indene oxalic ester, a substitute for linseed oil was produced with some measure of success.

²¹ German Pat. 254,767, Sept. 19, 1911.

²² U. S. Pat. 1,019,666, Mar. 5, 1912; Ger. Pat. 245,634, Jan. 4, 1911; Chem. Fabr. Worms A-G. German Pat. 348,088, Aug. 20, 1919.

²³ U. S. Pat. 1,133,432-3, Mar. 30, 1915.

²⁴ U. S. Pat. 1,370,195, Mar. 1, 1921.

²⁵ French Pat. 514,405; *Kunststoffe* 1922, 12, 70.

²⁶ U. S. Pat. 1,430,083, Sept. 26, 1922, and 1,481,801, Oct. 10, 1922.

²⁷ *Farbenfabrik vorm. F. Bayer und Co.*; German Pat. 305,515, Mar. 21, 1917; J. S. C. I. 1920, 165A.

Stern²⁸ found that cumaron or indene (not polymerized) either alone or when mixed with linseed oil could be used as a substitute for linseed oil. Later Darrin²⁹ found that cumaron resin which had been polymerized by heat, when mixed with linseed oil and naphtha, also could be used for this purpose.

Other Coating Compositions.

Lender³⁰ prepared a varnish base by heating cumaron resin (with or without the addition of oils) with sulphur or sulphur chloride³¹ under pressure. Schwarz³² treated hot cumaron resin with air or oxygen³³ under pressure and finally emulsified it with water using glue and potassium bichromate to prevent the separation of the emulsion. He stated that the solution can be used as a varnish.

The Koppers Company³⁴ produce a bituminous paint containing cumaron resin by heating coal tar pitch to 160-200° C., cooling the pitch to 150° C. and then adding a solvent containing the resin, or a solution containing cumaron and indene, which afterward is polymerized by heating in an autoclave.

Briggs³⁵ prepared an enamel consisting of cumaron resin, a pigment and an oil; suitable for use as a top coating on a slow drying paint or varnish. Robeson³⁶ has obtained an elastic waterproof coating, one component of which is cumaron resin, for use as a surfacing compound on brick, stone or iron. The composition is made up of the resin, a mineral or vegetable wax, a solvent for these and a pigment, preferably colloidal dust of silicon carbide.

Rubber.

The next most important use for cumaron resin thus far developed is in the production of rubber goods. Cumaron resin has a pronounced softening action upon rubber during the milling operation and the addition of a small quantity of the resin greatly facilitates handling of the rubber batch on the rolls. The milling of rubber involves the use of very heavy machinery and substantial labor and power costs. Reduction in the time of milling through the use of cumaron resin, therefore, is of significance for the rubber industry. Five per cent of the resin is sufficient for the purpose. The resin in crushed condition may be mixed with fragments of rubber or the resin in a molten state may be poured onto the rubber on the rolls. Cumaron resin is especially of utility in the production of light colored rubber compounds. In the manufacture of friction tapes the addition of cumaron resin is of decided advantage as it greatly increases the adhesive qualities of the tape. Cumaron resin is now used in making the sides of automobile

²⁸ German Pat. 345,816, Apr. 23, 1919; J. S. C. I. 1922, 41, 224A.

²⁹ U. S. Pat. 1,315,658, Sept. 9, 1919; 1,382,345, June 21, 1921.

³⁰ German Pat. 277,605, Feb. 8, 1913; Dutch Pat. 138, Mar. 2, 1914; Z. angew. Chemie, 1914, 27, 11.

³¹ See also Schlatter, U. S. Pat. 1,294,838, Feb. 18, 1919.

³² German Pat. 322,802, June 14, 1918; J. S. C. I. 1920, 728A.

³³ See also Knuppel (Ger. Pat. 253,427, May 2, 1912, J. S. C. I. 1912, 1190).

³⁴ Canadian Pat. 188,272, Jan. 14, 1919; Chem. Abs. 1919, 518; U. S. Pat. 1,292,907, and 1,292,908 of Jan. 28, 1919. (See Darrin, U. S. Pat. 1,296,776, Mar. 11, 1919; British Pat. 132,229, June 24, 1919; British Pat. 129,264, June 12, 1919; British Pat. 118,079, Dec. 14, 1917; Brit. Pat. 138,068, Dec. 30, 1919.)

³⁵ British Pat. 168,293, Feb. 3, 1921.

³⁶ U. S. Pat. 1,405,941, Feb. 7, 1922.

shoes, in rubber hose, rubber heels, gaskets and various types of mechanical rubber goods. However, the advantages in using the resin are not generally recognized by rubber manufacturers in this country and it is the author's belief that thorough tests by rubber technicians would greatly repay the industry by establishing the value of the resin as a means of improving rubber products and also reducing manufacturing costs.

Wells³⁵ proposed the use of cumaron resin in rubber compositions and he prepared a product suitable for making gaskets by mixing cumaron resin with rubber and fillers such as clay, asbestos, etc. The composition then was appropriately shaped and vulcanized.

Chicle Substitutes.

An important use for cumaron resin is in the preparation of chicle substitutes.³⁶ Cumaron resin mixes readily with chicle, pontianak rubber and rubber resin, and flavoring oils. The mass can be mixed with sugar solution and the mixture when properly prepared is free from any objectionable odor or flavor. Considerable quantities of the resin have been used for making chewing gum but, due to a slight change in the manufacture of the resin, difficulties were encountered by gum manufacturers. At the same time that trouble was experienced in preparation of the chicle substitute it was found that cumaron resin caused blooming in articles made from rubber. This difficulty in manufacture has now been overcome and cumaron resin will undoubtedly again come in use for the preparation of chicle substitutes just as it has been reinstated in the manufacture of rubber. While the purpose of use of cumaron resin in rubber and chicle substitutes is entirely different the cause of the failure in both cases was somewhat analogous. That is, the defective resin caused the sulphur in the rubber to bloom, while in the case of the chicle substitute it caused the sweetening incorporated with the chicle substitute to exude from the prepared chewing gum. The grade of cumaron employed in chewing gum should be one entirely free from heavy oils as these possess a tarry or aromatic taste which is disagreeable in chewing gum. A grade of cumaron resin has been produced which is free from oily substances produced by polymerization and this tasteless resin may be added to chicle in an amount ranging from 7 to 10 per cent. Larger proportions are not recommended.

Molded Articles.

Cumaron resin has found a somewhat limited use in the preparation of molded articles due to the nature of the material. Owing to brittleness and a low tensile strength the resin does not lend itself readily to this purpose. It has been used for the so-called cold molded products when mixed with other materials such as asphalt, petroleum pitch or gilsonite but its principal use in molding has been in the manufacture

³⁵ U. S. Pat. 1,248,226, Nov. 27, 1917; Chem. Abs. 1918, 12, 323.

³⁶ See Weber, U. S. Pat. 1,248,961, Dec. 4, 1917; and 1,402,817, Jan. 10, 1922.

of hot molded articles. (See Chaps. 24, 25 and 26.) Cumaron resin has several extremely valuable properties in that it is waterproof and has a high dielectric constant comparable with that of mica. Porcelain and gutta-percha are among the few materials used for electrical insulation which have a higher dielectric constant. The following table gives the comparative dielectric constant of cumaron resin with other insulating materials when measured under the same conditions.

Porcelain	5.73
Gutta-percha	4. -4.9
Cumaron Resin	3.5
Shellac	3.10
Vulcanized Rubber	2.69
Rosin	2.5
Rubber	2.12

Baekeland³⁷ first proposed the addition of cumaron resin to products made by reacting phenol or phenolic alcohols with formaldehyde. McCoy³⁸ used cumaron resin as a binder when preparing molded articles from asbestos, silica, wood flour, etc., in addition to polymerized vegetable oils such as china wood oil, or sterculia oil. He first preshaped his molding compound to the desired form and then by means of pressure and heat formed the finished molded article. Or the operation was carried out by the so-called cold molding process but in this case less vegetable oil was used in the composition. When manufactured in the latter way, the articles are finally subjected to a baking treatment³⁹ which serves to polymerize the binders.⁴⁰ By grinding a mixture of cumaron resin and filling material with water, Gudge⁴¹ found that some difficulties encountered when using resinous binders for the preparation of molded articles were overcome. Without the use of water, the resin normally "balls" with the filler or, if a ball mill is used, the mix adheres to the side of the mill so that an uneven composition is obtained. Wells⁴² made a molded electric insulator using cumaron resin as a binder. Abrasive articles such as grinding wheels are made by Power from abrasive grains bonded with cumaron resin and shellac. The molded products are baked to cause hardening.⁴³

An elastic cement suitable for use as a cement for electric vacuum apparatus and other purposes has been made by McCoy⁴⁴ by mixing gutta-percha and cumaron resin.

³⁷ U. S. Pat. 1,038,475, Sept. 10, 1912.

³⁸ U. S. Pat. 1,268,031, May 28, 1918.

³⁹ Can. Pat. 187,645, Oct. 20, 1918.

⁴⁰ See also U. S. Pat. 1,299,846, Apr. 8, 1919; 1,300,218, Apr. 8, 1919; U. S. Pat. 1,245,363, Nov. 6, 1918; Reissued Pat. 15,199, Sept. 20, 1921.

⁴¹ U. S. Pat. 1,299,706, Apr. 8, 1919.

⁴² U. S. Pat. 1,332,860, Mar. 2, 1920.

⁴³ U. S. Pat. 1,427,844, Sept. 5, 1922.

⁴⁴ U. S. Pat. 1,236,190, Aug. 7, 1917; Chem. Abs. 1917, 2722.

shoes, in rubber hose, rubber heels, gaskets and various types of mechanical rubber goods. However, the advantages in using the resin are not generally recognized by rubber manufacturers in this country and it is the author's belief that thorough tests by rubber technicians would greatly repay the industry by establishing the value of the resin as a means of improving rubber products and also reducing manufacturing costs.

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³⁶ See Weber, U. S. Pat. 1,248,961, Dec. 4, 1917; and 1,402,817, Jan. 10, 1922.

Paper Size.

Cumaron resin has been used in the preparation of sizing for paper but it has not readily lent itself to this purpose because of its unsaponifiable properties. The usual method of preparing paper size with cumaron resin is first to mix the resin with a saponifiable resin or fat such as rosin or stearic acid and upon saponifying the resulting mixture by means of an alkali an emulsion with water can be prepared. The emulsified mixture is then added to the pulp from which the paper is to be prepared and calendered in the usual manner.⁵⁰ Later researches have developed a product of cumaron and indene which is capable of being emulsified, using certain clays as the emulsifying agent, and this material has been used for the preparation of paper on a laboratory scale. It has not, however, as yet come into extended commercial use.

According to the Rutgerswerke Akt. Ges.⁵¹ by melting cumaron resin with salts which promote emulsification, such as the alkali salts of sulphonated aromatic and naphthenic acids, a mixture is obtained which can be readily emulsified. Also aromatic or naphthenic compounds can be first mixed with the resin, the mixture sulphonated and then neutralized and the same result obtained. The resulting emulsion is used for sizing paper or other fibrous material.

Felt and Cloth Sizing.

A somewhat similar use to the sizing of paper was found by Perry.⁵² He prepared roofing felts by impregnating the watery pulp of beaten rags with an emulsion composed of cumaron resin and a saponified resin. The pulp was then dried in a continuous sheet by means of rolls but was not calendered as heavily as in the manufacture of paper. Roether⁵³ used a kindred emulsion for the waterproofing of cloth. To a soap solution consisting of saponified cocoanut oil and tallow he added paraffin, cumaron resin and linseed oil while the solution was being agitated and boiled. Cloth was immersed in the warm emulsion, wrung out and calendered, the finished cloth being thus rendered waterproof.

Printing Inks.

Still another use for cumaron resin has been found in the preparation of printing inks but in this case its use is dependent upon the relative price of the resin and linseed oil. While there are advantages in the use of cumaron resin for this purpose, such as improvement in the lustre of the printed matter and an increase in the stability of colors in the ink, these advantages have not been of sufficient im-

⁵⁰ Lender, British Pat. 17,576, Dec. 16, 1915; see also patent to Muth, U. S. Pat. 1,194,866, Aug. 15, 1916; and Ellis, U. S. Pat. 1,007,681, Nov. 7, 1911.

⁵¹ Ger. Pat. 348,063, Sept. 6, 1918; J. S. C. I. 1922, 41, 382A.

⁵² U. S. Pat. 1,302,209, April 29, 1919.

⁵³ U. S. Pat. 1,414,670, May 2, 1922.

portance to offset the question of price. The resin will undoubtedly come into more extended use for this purpose if producing costs can be lowered or, on the other hand, if the price of linseed oil increases substantially.

Tanning Liquor.

Cumaron resin has been proposed by Renner and Moeller⁵⁴ for use in the preparation of tanning liquors. They found that by condensing and sulphonating cumaron resin mixed with aromatic substances such as phenols and then oxidizing the product to quinone-like compounds a tanning agent was obtained. The condensation may be brought about with formaldehyde.

By-products of Cumaron Resin.

The light oils obtained in the production of cumaron resin have found but little industrial use and Lillienfeld⁵⁵ proposes using the by-product oils obtained by the vacuum distillation of cumaron resin as lubricating oil, insulating material, transformer oil and for pharmaceutical purposes. The yellow viscous fluorescent oil boiling between 150 and 300° C. in vacuo is the material preferred for this purpose. Dennis⁵⁶ prepares a cleansing solution by emulsifying with water and a soap, the by-product oils obtained in the production of cumaron resin.

Tar Acid Resin.

Acid resins obtained from the sulphuric acid used in washing light oils of coal tar are not, strictly speaking, cumaron resins, but as they are not unrelated brief mention will be made of such products in this chapter. The acid resins are usually obtained by adding water to the sulphuric acid used in refining coal-tar oils and then heating the dilute solution without carbonizing the resins present. The dilute acid solution is extracted with a hydrocarbon such as benzol and the resin separated by evaporation of the solvent or the benzol solution may be utilized by adding it to solutions of other resins.

Hilpert⁵⁷ obtained a resin as described above and found the product suitable for use as the base of a quick-drying lacquer. Later⁵⁸ he obtained the resin as a bright yellow powder from the sulphuric acid used in refining benzol. From acid used to refine naphthalene⁵⁹ the resin derived was dark brown in color.

Thorp and Thorp⁶⁰ separate the acid resins from the dilute sulphuric acid by washing the pasty residue obtained after separating the bulk of the solution with water. The mass is then steam distilled and the resinous mass again washed, neutralized with alkali if necessary, and dried. Schummer⁶¹ distills

⁵⁴ British Pat. 148,750, June 26, 1920; J. S. C. I. 1922, 47, 185A.

⁵⁵ British Pat. 163,271, May 21, 1920; J. S. C. I. 1922, 47, 50A.

⁵⁶ U. S. Pat. 1,365,464, Jan. 11, 1921.

⁵⁷ German Pat. 324,722, Nov. 28, 1916; U. S. Pat. 1,427,386, Aug. 29, 1922; J. S. C. I. 1920, 792A; Brit. Pat. 157,715 Jan. 10, 1921.

⁵⁸ German Pat. 319,010, Apr. 4, 1916; 319,011, Dec. 5, 1916; J. S. C. I. 1920, 16, 577A; see also German Pat. 341,693, Apr. 11, 1917; J. S. C. I. 1922, 47, 23A.

⁵⁹ German Pat. 320,808, Dec. 9, 1916.

⁶⁰ British Pat. 124,605, Apr. 13, 1918; Chem. Abs. 1919, 13, 1760.

⁶¹ German Pat. 320,255, May 7, 1918; J. S. C. I. 1920, 633A.

the pasty resinous mass obtained in a similar manner in vacuo, the sulphur dioxide fumes being recovered and converted into sulphuric acid.

Brooks and Humphrey⁵³ state that crude benzols from coal-gas tar, carbureted water-gas tar, or "holder oil" and Pintsch gas "hydrocarbon drips" are noted for the relatively large per cent of so-called unsaturated paraffins which they contain. After treating such benzols with sulphuric acid, and washing neutral with alkali, it is always noted that on redistilling the treated oil large quantities of sulphur dioxide are evolved accompanied by blackening of the still residues. These still residues are high boiling viscous oils which on prolonged heating are convertible into pitch or resin, which some manufacturers erroneously designate as "cumaron resin." It is much more probable that they are highly polymerized products derived in part from cyclopentadiene and similar diolefin hydrocarbons. Diolefins are known to give resinous polymers which contain sulphur.

Wirth⁵⁴ obtained resinous bases from coal tar and other tar oils boiling above 300° C. He first freed the tar of phenols by means of a solution of caustic soda and after separation of the alkaline solution extracted the resinous bases by agitating the tar oil with dilute sulphuric acid having a specific gravity of 1.12. The acid solution was allowed to settle, and separated. The lower boiling resinous bases are recovered from the dilute acid solution by means of caustic soda, while the higher boiling resins separate from the tar on cooling. The consistency of the resin bases varies from a yellow oil to a solid reddish brown substance and they boil above 300° C. Their acid salts form insoluble compounds with phenol and its homologues.

Identification of Cumaron Resin.

The detection of cumaron resin when mixed with other resins in varnishes is a problem which often confronts chemists having to do with products of this nature. Its separation and identification is comparatively simple, due to several of its well known distinctive properties. It is not safe to conclude that cumaron resin is present by determining one or two properties of the resin in question as there are certain other resins which have somewhat similar properties and reactions.

Cumaron resin⁵⁴ dissolves completely or almost completely in acetone while coal-tar pitch, lignite pitch, wood-tar pitch and petroleum pitch are practically insoluble in this solvent. Phenol-aldehyde resins, or as they are commonly though incorrectly called phenol condensation products, are insoluble in petroleum spirits, while cumaron resin is partially soluble. Furthermore the phenol-aldehyde resins yield quantities of phenols on treatment with soda lime⁵⁵ while cumaron resins yield only traces of these bodies. Natural resins for the most part melt at higher temperatures and, with the exception of pontianac resin, have a higher acid number, saponification and iodine values, besides being optically active. The separation from fatty acids can be accomplished by esterification⁵⁶ the esters being removed by distillation or extraction with alcohol. Oxidized oils seriously interfere with this

⁵³ J. Am. Chem. Soc. 1918, 853.

⁵⁴ U. S. Pat. 1,339,310, May 4, 1920.

⁵⁵ Marcusson, J. S. C. I. 1919, 329A; Chem. Zeit. 1919, 43, 109 and 122; Chem. Abs. 1919, 2607.

⁵⁶ This is not a characteristic test for phenol-aldehyde resins.

⁵⁷ Wolff. Farb. Z. 1918, 23, 307.

separation, however, so saponification of the fatty acids is resorted to, the soaps being separated by boiling with water.

The final identification of the resin is made by destructively distilling the resinous material remaining after the above treatment. Cumaron resin decomposes at 300–400° C. with the formation of cumaron B.P. 172, indene B.P. 182, hydrindene B.P. 176 along with a small quantity of cresols, phenols, etc. By fractionally distilling the distillate obtained from the destructive distillation of cumaron resin the largest fraction boils between 168–180° C. Pontianac resin as well as some other resins will give a smaller fraction boiling at this range and it is therefore advisable to determine the presence of cumaron and indene in the distillates by means of their picrates and bromides; cumaron picrate melting at 102–103° C., the monobromide at 39° C., the dibromide at 86° C. The boiling point of indene picrate is 179.5–180.5° C. while the dibromide melts at 43–45° C.

A more rapid method of determining the presence of cumaron resin is by a color reaction with bromine. Cumaron resins will give a permanently red color when treated with bromine in a solution of dry chloroform in the presence of glacial acetic acid. Pontianac resin will color the solution yellow though there may be a slight red tint to the solution when the bromine is first added. It is therefore advisable to check the color after the solution has stood for some time, preferably 24 hrs. Usually 1 hour's time is sufficient to develop the color definitely except when pontianac resin is present in large proportions, and in this case it is preferable to resort to the destructive distillation of the resin with the subsequent identification of cumaron and indene in the distillate as given above.

The test is carried out as follows: 1 cc. of a 10 per cent solution of the resin in chloroform is diluted with 6 cc. of a chloroform and 1 cc. of glacial acetic acid is added. The solution is then shaken or stirred and 1 cc. of a 10 per cent solution of bromine in chloroform is added, the solution again shaken or stirred, the container corked and allowed to stand; the presence of cumaron resin being indicated by the permanent red color of the solution.

A chart follows showing the color changes which take place when mixtures of cumaron resin and pontianac resin are treated in accordance with the above procedure.

Sample	On add. of Br. sol.	After Standing ½ hr.	Standing 1 hr.	Standing 24 hrs.	Standing 96 hrs.	Standing 30 days
Cumaron Resin red	red	red	dark red	dark red	dark red
50% Cumaron } 50% Pontianac } red	red	red	red	red	red
10% Cumaron } 90% Pontianac } orange red	orange red	orange red	orange red	orange red	orange red
Pontianac yellow orange	yellow orange	yellow orange	yellow	yellow	yellow

Another rough test is to treat the distillate boiling at 170–180° C. obtained from the destructive distillation of the resin in question with a few drops of concentrated sulphuric acid. The presence of cumaron and indene is indicated when the distillate is transformed into a viscous polymerized mass, though this should by no means be taken as being conclusive.^{66a}

The foregoing method of separating and identifying cumaron resin was developed and successfully used in the author's laboratory.

^{66a} Wolff, *Farben Z.* 1918, 23, 307.

Acid Resin in Cumaron Resins.

Inferior resins of European make were studied by Wolff.⁷⁷ From samples having acid numbers ranging from 5 to 12 he isolated 4 to 9 per cent of acid resins. The acid resins are dark colored substances, insoluble in petroleum ether but soluble in benzol, ether, ethyl alcohol and acetone. On heating the acid resins to 100° C. the acid numbers decreased but their saponification numbers increased rapidly, apparently being due to the formation of anhydrides. Upon exposing the acid resins to esterifying conditions⁷⁸ he obtained esters.

Acid in Cumaron Resin.

Earlier, Wolff⁷⁹ had devised a method of separating free sulphuric and sulphonic acids from cumaron resin. He extracted the substances by treating a solution of cumaron resin dissolved in neutral benzol with successive portions of warm water and precipitated the acids by means of barium chloride.

⁷⁷ Farben Z. 1918, 23, 307; Chem. Abs. 1919, 2138, J. S. C. I. 1919, 646A.

⁷⁸ See Wolff, Chem. Abs. 1915, 8, 2495.

⁷⁹ Farben Z. 1917, 919.

Chapter 4.

Modern Methods of Producing Cumaron Resin.

The preceding chapters have indicated the numerous methods which have been proposed for preparing cumaron resin. The present chapter is devoted to methods by which cumaron resin is manufactured at the present time. As the production of the resin in the United States represents a comparatively recent development, the practical methods adopted in this country to a considerable extent reflect the practice in those countries where the industry was earlier established.

In manufacturing cumaron resin the following items of procedure will be considered.

1. Refining the solvent naphtha.
2. Drying the naphtha.
3. Polymerization.
4. Separation of tar.
5. Neutralization.
6. Washing the resin-containing oil.
7. Distillation.

Refining the Solvent Naphtha.

Crude coal tar is fractionally distilled and the hydrocarbon fraction boiling between 150 and 200° C. (German practice) constitutes the raw stock of the present operation. Sometimes a closer fraction of boiling point ranging from 160° to 180° C.¹ This is the usual practice in the United States as the more desirable resins are produced from cumaron and indene. The fraction obtained from the first distillation contains too many impurities and hence should be very carefully redistilled or rectified. This is best carried out in column stills. All substances which would be acted upon by the polymerizing agent—sulphuric acid—should be eliminated to as great an extent as possible. Benzol, toluol, xylols, naphthalene, etc., are removed to advantage. Tar acids should not be present. Only by starting with a sharply fractionated naphtha can high grade resin be obtained. Naphtha which has been properly rectified should yield from 25 to 40 per cent of polymerizable material.²

¹Rabinovitz, U. S. Pat. 1,416,062, May 16, 1922. The fraction 165-185° C. also has been recommended.

²Barrett Co. Brit. Pat. 142,806, Apr. 28, 1920; Miller, U. S. Pat. 1,360,663, Nov. 30, 1920.

Drying the Naphtha.

Naphtha usually contains water or moisture which would dilute the acid used in polymerization and render the result uncertain. Naphtha may be dried by various drying agents, the most readily available being sulphuric acid. A sufficient quantity of acid is mixed with the naphtha to unite with the moisture and settle to the bottom where the diluted acid is drawn off. The strength and amount of the acid which is added should be proportioned to the quantity of water present to result in dilution of the acid below the polymerizing strength. Three to five gallons of 60° sulphuric acid usually will suffice to dry 1000 gallons of naphtha.³ This quantity of acid is agitated with the naphtha, settled and drawn off. The drying step is best carried out in a lead-lined tank or stoneware receptacle equipped with an agitator. Drying also may be carried out in the same receptacle as that used for polymerization. If the latter is of iron or steel there is some danger, however, that iron may be dissolved by the diluted acid and contaminate the resin. Hence a separate drier is preferable.

Polymerization.

Foreign experience has shown that certain factors play an important rôle in the manufacture of high grade resin.

To find widespread use the resin must be light in color, hard and possessed of a high melting point. A dark-colored soft sticky resin has comparatively few uses. One of the largest outlets for cumaron resin is in the production of varnishes. In the selection of his raw material the varnish maker is very critical of color. Hence the mere production of a polymerized product will not suffice. It must possess a standard of quality comparable with the best natural resins.

Heat Evolution.

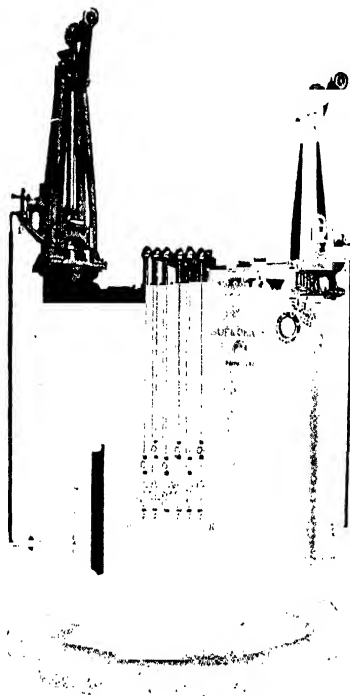
The polymerizing action of sulphuric acid is an exothermic one (see Chap. 2), there being a very rapid development of heat immediately the acid comes into contact with the polymerizable bodies due principally to the indene present. This rise in temperature is objectionable because of possible discoloration of the resulting resin. Solvent naphtha containing only a small proportion of polymerizable bodies does not become strongly heated during polymerization as the presence of a large amount of inert hydrocarbon acts as a diluent and serves to some extent as a heat regulator.⁴ The conditions are different, however, when treating naphtha containing 30 or 40 per cent of polymerizable bodies. As may be expected the heat evolution in such a case is very great and efficient cooling during the progress of the reaction therefore is necessary.

³ Miller, U. S. Pat. 1,360,665, Nov. 30, 1920.

⁴ J. Ind. Eng. Chem. 1916, 797.

Rapidity of Mixing.

A short period of contact of the acid with the naphtha also is conducive to the production of a light-colored resin. But a short time of contact, if polymerization is to be effective, means the evolution of excessive localized heat from oils rich in cumaron and indene. Hence resort should be made to violent agitation and strong cooling in order to secure rapid mixing and polymerization while quickly dissipating the heat evolved.



Courtesy of Buffalo Foundry & Machine Co.

FIG. 2.—A Type of Mixer Applicable in the Production of Cumaron Resin.

A high velocity of reaction, or, more properly speaking, a quick performance of the reactions in order to secure a hard, light-colored resin, necessitates very careful control over the exothermic reaction involved.

Mixing Devices.

Being much denser than the naphtha the acid settles rapidly when added to the former and an ordinary paddle agitator is not as satisfactory a mixing device as one which constantly elevates the acid from bottom to the top of the naphtha layer. A rapidly revolving vertical

conveyor enclosed by a tube open at either end serves to accomplish the mixing. Mixing also may be carried out in a tank equipped with a pump which draws the naphtha and acid from the bottom and returns the mixture to the top of the tank. (See Fig. 2.) This type of apparatus is commonly used for mixing materials of different densities. The agitating device should be powerful and the cooling means adequate. The polymerizer advantageously is filled with cooling pipes through which is passed cold water, or, which is better, brine from a refrigerating plant.

Sulphuric Acid Requirement.

For each 1000 gallons of naphtha containing 30 to 40 per cent or thereabouts of polymerizable constituents from 30 to 50 gallons of 66° sulphuric acid⁵ will be required. As the oil polymerizes, its specific gravity increases and this change may be used as a means to determine the progress of the reaction. When two successive samples drawn from the polymerizer after an intermediate addition of acid show the same specific gravity the polymerizing action is at an end.

Temperature Control.

Thus the procedure recommended is to run the dried naphtha from the drying tank into the polymerizer and to cool the oil as much as possible with the cooling means at hand. With brine refrigeration this may be -5 or -10° C. The agitator being in motion, the charge of 66° acid is run slowly into the naphtha, or is added in small portions to the latter, while the operator constantly watches the thermometer. If the temperature rises too rapidly, the addition of acid must be checked. The temperature should not rise above $+10$ or $+15^{\circ}$ C. for the production of the highest grade of resin. To obtain pale colored resin Miller⁶ states the temperature should not rise above 20° C.

It may be thought that the temperature could be regulated better by using weaker acid but acid of a lesser strength than 66° apparently does not afford a sufficiently hard resin.⁷ Wendriner recommends treating naphtha with 60° acid and after the acid is well emulsified with the oil to add a small amount of 66° sulphuric acid to initiate the reaction of polymerization. Three to five per cent of 60° and one-fourth of one per cent of 66° acid by volume are used. Polymerization sets in violently and the temperature of the oil is allowed to rise to over 100° C. By this notable rise in temperature a better degree of polymerization is obtained than when cooling is employed. On the other hand, when using 60°, then 66° acid, with *cooling*, a softer grade of resin than is desired results. Wendriner finds the treatment with weaker then stronger acid to eliminate tar. Although this feature is of advantage, it is doubtful if the softer quality of resin

⁵ Miller, U. S. Pat. 1,360,665, Nov. 30, 1920.

⁶ U. S. Pat. 1,360,665, Nov. 30, 1920.

⁷ Ger. Pat. 281,432, Nov. 8, 1918.

obtained compensates for this simplification of manufacturing operation. Also, since a high temperature tends to yield a darker colored resin, the employment of 66° acid with cooling is a more practical method. Acid of a substantially higher strength than 66°, for example, 98 per cent (see Chap. 2), is not recommended. Acid of this higher strength forms excessive amounts of tar and insoluble products and is liable to discolor the resin. Furthermore there is always the danger of forming excessive amounts of sulphonic acids, with consequent reduction in yield. Acids stronger than 66° doubtless could be used by establishing extreme cooling conditions coupled with very slow addition of the reagent. Practical considerations involving several factors thus far have not justified this procedure.

Removal of Tar.

After the polymerization stage is completed, the oil is allowed to stand for a short time in order that the tar or sludge may settle. Complete removal of the tar is essential in order to preserve the color of the resin. The tar obtained when using 66° acid is stiff and heavy and is drawn off from the oil with more or less difficulty. The tar normally amounts to about 1 or 2 per cent of the original naphtha.

Neutralization.

The oil is then pumped to a neutralizing tank where a solution of caustic soda of specific gravity 1.2 or 1.3 is added to neutrality or even faint alkalinity.⁸ If a careful separation of the sludge has been made, the amount of caustic soda required should not exceed 1 or 2 per cent. In order to avoid the time required to discharge the contents of the polymerizer into the neutralizing tank with consequent more protracted contact of the oil and acid, the neutralization may be conducted in the polymerizer.

Generally, however, it is preferable to accomplish the neutralization in a separate receptacle in which the washing is carried out.

Washing.

The oil is washed with several changes of water until most of the soluble matter (principally sodium sulphate and sulphonate) is extracted. The washing tank should be equipped with stirrers or a compressed air line for purposes of agitation. If sodium sulphate in any appreciable quantity remains in the resin, the color of the latter may change on standing, a whitish product resulting. Also water-soluble material in a resin used in varnish making is undesirable, hence the washing should be thorough. Cumaron resin of an ash content of less than 0.1 of one per cent is specified for some purposes. After washing, the oil is allowed to stand for some time to allow the water to settle. Some loss of course occurs in the several settling and sepa-

⁸ Miller, U. S. Pat. 1,360,665, Nov. 30, 1920.

conveyor enclosed by a tube open at either end serves to accomplish the mixing. Mixing also may be carried out in a tank equipped with a pump which draws the naphtha and acid from the bottom and returns the mixture to the top of the tank. (See Fig. 2.) This type of apparatus is commonly used for mixing materials of different densities. The agitating device should be powerful and the cooling means adequate. The polymerizer advantageously is filled with cooling pipes through which is passed cold water, or, which is better, brine from a refrigerating plant.

Sulphuric Acid Requirement.

For each 1000 gallons of naphtha containing 30 to 40 per cent or thereabouts of polymerizable constituents from 30 to 50 gallons of 66° sulphuric acid⁵ will be required. As the oil polymerizes, its specific gravity increases and this change may be used as a means to determine the progress of the reaction. When two successive samples drawn from the polymerizer after an intermediate addition of acid show the same specific gravity the polymerizing action is at an end.

Temperature Control.

Thus the procedure recommended is to run the dried naphtha from the drying tank into the polymerizer and to cool the oil as much as possible with the cooling means at hand. With brine refrigeration this may be -5 or -10° C. The agitator being in motion, the charge of 66° acid is run slowly into the naphtha, or is added in small portions to the latter, while the operator constantly watches the thermometer. If the temperature rises too rapidly, the addition of acid must be checked. The temperature should not rise above $+10$ or $+15^{\circ}$ C. for the production of the highest grade of resin. To obtain pale colored resin Miller⁶ states the temperature should not rise above 20° C.

It may be thought that the temperature could be regulated better by using weaker acid but acid of a lesser strength than 66° apparently does not afford a sufficiently hard resin.⁷ Wendriner recommends treating naphtha with 60° acid and after the acid is well emulsified with the oil to add a small amount of 66° sulphuric acid to initiate the reaction of polymerization. Three to five per cent of 60° and one-fourth of one per cent of 66° acid by volume are used. Polymerization sets in violently and the temperature of the oil is allowed to rise to over 100° C. By this notable rise in temperature a better degree of polymerization is obtained than when cooling is employed. On the other hand, when using 60°, then 66° acid, with *cooling*, a softer grade of resin than is desired results. Wendriner finds the treatment with weaker then stronger acid to eliminate tar. Although this feature is of advantage, it is doubtful if the softer quality of resin

⁵ Miller, U. S. Pat. 1,360,665, Nov. 30, 1920.

⁶ U. S. Pat. 1,360,665, Nov. 30, 1920.

⁷ Ger. Pat. 281,432, Nov. 8, 1918.

Chapter 5.

Resins from Petroleum. Polymerization of Certain Unsaturated Hydrocarbons.

In this chapter are included a series of resinous substances derived from various unsaturated hydrocarbons, particularly those obtained from petroleum. Artificial asphalts are given only very brief mention as these are thoroughly covered in other treatises. Many bitumens are altered by simple heat treatment forming products sometimes called artificial asphalts but this class is omitted here because its discussion would lead too far from the subject of synthetic resins proper.¹ Tars and pitches which are hardened by chemical treatment—with acids, sulphur, lime and the like—do, however, receive brief consideration. A more detailed discussion of resins and asphalts made by the action of sulphur is to be found in Chapter 10. Resins obtained by the action of sulphuric acid and other polymerizing agents on the cumaron and indene of solvent naphtha and coal-tar oils are treated in Chapters 2-4. Other unsaturated hydrocarbons, such as the dienes of cracked petroleum, are included in the present chapter. In the main, the products considered under this heading are of low grade, many being dark brown or black in color, soft or excessively brittle substances, limiting their uses to the production of cheap varnishes, roofing compounds and in making pavements.

Polymerizing Effect of Silent Electric Discharge.

The silent electric discharge is a most energetic polymerizing agent. Its characteristic action on organic compounds is that of condensation and polymerization to yield substances of very high molecular weight, which probably have a cyclic structure. Although thus far given very little consideration as a means of technical production of synthetic resins, a systematic investigation with this instrumentality should be forthcoming. In illustration of some of the changes produced by the silent electric discharge the work of Losanitsch² may be consulted. He obtained a brown solid from carbon disulphide. From the disulphide and ethylene, there was produced a brownish yellow insoluble mass having the composition $5\text{CS}_2 \cdot 2\text{C}_2\text{H}_4$. Acetylene likewise combined with carbon disulphide to form a black insoluble solid $3\text{CS}_2 \cdot 2\text{C}_2\text{H}_2$.

¹ Blown petroleum asphalts are fully discussed in Chapter 18 of Abraham's *Asphalts and Allied Substances*, New York, 1920.

² Ber. 1907, 40, 4656.

Acetylene.

This gas quickly condenses under the action of the silent electric discharge, forming first a thick liquid and then a solid substance. By extraction with ether or alcohol the condensed acetylene may be separated into two portions, a soluble, viscous oil and an insoluble solid which constitutes the major part. Both portions decompose violently when heated above 100° C. with the formation of tarry bodies and carbon.³ The condensation product takes up oxygen, the liquid portion becoming a solid, transparent resin. Solid substances also are obtained from acetylene and ethylene, acetylene and hydrogen sulphide, acetylene and carbon monoxide, and acetylene and sulphur dioxide. With acetylene and hydrogen a black resin is formed. Carbon monoxide and carbon disulphide yield a brown, insoluble body, $3\text{CS}_2\cdot\text{CO}$. The contact of acetylene with hot copper oxide yields cuprene which has a voluminous character if the length of heating is short but if heating is continued for 6-8 hours the product is a cork-like solid.⁴

Condensation of Mixed Olefines.

Ethylene hydrocarbons condense with diolefines in the presence of certain anhydrous inorganic chlorides as catalysts, forming oils and resins.⁵ Thus, amylene, diamylene, menthene, pinene, camphene and styrene (styrol) unite with hydrocarbons containing at least two double linkages in the molecule, e.g., butadiene (erythrene) isoprene, dipentene or phellandrene; the reaction being more pronounced when conjugated ethylene bodies (conjugated dienes) are employed. This is to be expected from the general instability of the conjugated structure—the readiness with which compounds of this type oxidize and polymerize. As catalysts, anhydrous aluminum chloride and ferric chloride, boron trichloride and magnesium chloride are effective. A mixture of 10 parts of cycloheptatriene and 50 parts of trimethylethylene is treated with anhydrous ferric chloride, the latter being added in small portions with cooling. The mixture is allowed to stand at room temperature for 24 hours. Any unchanged hydrocarbon is removed by distillation and the residue is extracted with ether. The ether-soluble portion is a sticky solid, the insoluble portion is a yellow, pulverizable product. Equal parts of camphene and isoprene treated with 5 per cent of aluminum chloride and extracted with ether yield a soluble portion which is a soft solid and an insoluble residue which is white or light yellow, easily pulverized and insoluble in most of the common solvents.⁶

³ Note also Berthelot, *Compt. rend.* 1898, 126, 567.

⁴ Kaufmann and Schneider, *Ber.* 1922, 55B, 267.

⁵ Schering, J. S. C. I. 1915, 238; German Pat. 278,486, May 24, 1913.

⁶ Anhydrous aluminum chloride converts amylene into a heavy oil and various other ethylene hydrocarbons and terpenes into balsam-like products. *Ann.* 1902, 324, 23; *Ber.* 1909, 42, 4610, 4613. In the endeavor to obtain isoprene by heating acetylene and propylene under pressure polymerization occurs in part

Ozonized Products.

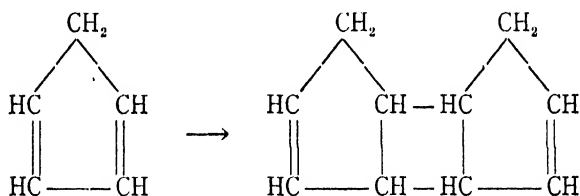
Ozone reacts with ethylene hydrocarbons forming ozonides which readily polymerize in some cases to solid gummy or glassy substances. The explosive character of ozonides is such as to deter usage in the synthetic resin field. The subject of ozonides has been summarized by Harries.⁷

Butadiene and Boron.

Butadiene or a homologue is polymerized, according to Bayer,⁸ by addition of a halide of boron, or a mixture of boron halides, with or without the use of a diluent. The products are viscous, plastic, or brittle, according to the temperature and amount of boron halide used. They serve as substitutes for resins.

Pentadiene.

Cyclopentadiene⁹ upon standing at room temperature goes over into dicyclopentadiene



By heating under pressure dicyclopentadiene continues to polymerize until it is converted into a hard resin somewhat resembling amber. Crude benzols according to Brooks¹⁰ contain cyclopentadiene and similar diolefin hydrocarbons which are converted to resins by sulphuric acid. The strong acid acts explosively with carbonization, resinous bodies being produced by the diluted acid.¹¹ Kronstein¹² heated pure cyclopentadiene in a closed tube to 160° C. After 5 hours' heating the liquid became turbid and a white powder separated. This change continued until all of the liquid was converted into an opaque solid, a polycyclopentadiene.

to bodies capable of use as varnish or turpentine substitutes. Traun, British Pat. 156,116, 1920; J. S. C. I. 1922, 41, 436A. Note also Plauson, U. S. Pat. 1,436,819, Nov. 28, 1922.

⁹Ann. 1905, 343 311; 1910, 374, 288; 1912, 390, 236; 1915, 410, 1. Koetschau, Z. angew. Chem. 1922, 35, 509; Chem. Abs. 1923, 337.

⁸J. S. C. I. 1913, 1078; German Pat. 264,925, April 16, 1912. F. Bayer & Co.

⁷Gurwitsch, Wissenschaftliche Grundlagen der Erdölbearbeitung 1913, 48.

¹⁰Brooks and Humphrey, J. Am. Chem. Soc. 1918, 854.

¹¹Kraemer and Spilker, Ber. 1896, 29, 554.

¹²Ber. 1902, 35, 4151.

Chlorocyclopentene.

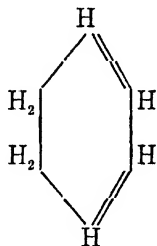
The treatment of cyclopentadiene with dry hydrogen chloride yields a monocyclopentene (C_5H_7Cl), a highly refractive liquid which on standing, even in the absence of air and light, becomes resinous with the formation of hydrogen chloride. Concentrated sulphuric acid acts explosively on the chlor compound.

Chlorinated Cyclopentane from Petroleum.

By chlorinating the portion of Caucasian petroleum boiling from 68° to 73° C. dichlormethyl cyclopentane is produced and this substance when diluted with glacial acetic acid and resinified with a small amount of sulphuric acid has properties similar to the polymerized hexadienes described below.¹³

Dihydrobenzene Resins.

Benzene adds hydrogen to form dihydrobenzene (cyclohexadiene) and tetrahydrobenzene. These ring compounds behave in a manner similar to olefines. Dihydrobenzene, dihydrotoluene and the bromination products of the latter polymerize or become resinous on exposure to sunlight, or when distilled or even when allowed to stand for a considerable time. Resins form from dihydrobenzene by oxidation in a fashion similar to the manner in which terpenes oxidize. With sulphuric acid in considerable proportion, the reaction is very violent, resins or tars being produced.¹⁴ More useful grades of resin are obtained by treatment with milder agents of polymerization, or the employment of very small proportions of vigorous activators of polymerization.¹⁵ These resins are odorless and generally light in color. From Δ -1-3 dihydrobenzene diluted with glacial acetic acid, a resin



is obtained by boiling with a few per cent of sulphuric acid. The procedure is to boil for 7 hours, 200 parts of the dihydrobenzene, 500 parts acetic acid and 5 parts sulphuric acid (97 per cent). The acetic acid is removed by distillation in vacuo and the sulphuric acid by washing with water and mild alkali. A clear glassy solid results, which is soluble in turpentine or benzol. Aluminum chloride also has pronounced polymerizing properties. Six parts of the anhydrous com-

¹³ Badische, German Pat. 263,159, 1912; British Pat. 23,543, 1912.

¹⁴ Baeyer, Ber. 25, 1841.

¹⁵ Badische, German Pat. 263,159, 1912; British Pat. 23,543, 1912.

pound are added slowly with cooling to 30 parts of dihydrobenzene, the mixture heated to 40° C. until reaction ceases. The mass is extracted with benzol, the extract washed with soda solution and the benzol driven off, leaving a nearly colorless resin. Or the reaction mixture is washed with dilute hydrochloric acid and the resin distilled with steam. By the same procedure, resins may be prepared from 1-methyl- Δ -1-3-dihydrobenzene. Alkali metal also may be employed as a polymerizing agent.

Dichlor Cyclohexane.

A mixture of 100 parts of 1-2 dichlor cyclohexane, 200 parts of glacial acetic acid and 20 parts of zinc chloride is boiled and hydrogen chloride is copiously evolved. The reaction mixture is cooled and filtered to collect the resinous precipitate. This is washed and dried.

Resins from Cracked Oils.

Petroleum oils subjected to the cracking process in the production of gasoline form certain unstable hydrocarbons of an unsaturated character which resinify on standing, especially when in contact with air. Ellis and Wells¹⁶ have studied these resins, particularly from the standpoint of petroleum refining.

Highly cracked oils especially are prone to leave a thick resinous deposit on slow evaporation in air. Brooks¹⁷ thinks these resin-forming bodies are probably conjugated unsaturated hydrocarbons, illustrated by isoprene, dimethylhexadiene, cyclohexadiene and the like which are known to resinify in contact with air. These conjugated diolefines also react very energetically with concentrated sulphuric acid, and this behavior is particularly pronounced in crude benzol from water-gas tar, the light condensate from Pintsch gas and the like. That ordinary unsaturated hydrocarbons containing one double bond do not exhibit this behavior, Brooks observes, has been definitely established—in fact, even pure olefines, with no saturated hydrocarbons present, do not yield tars with ordinary concentrated sulphuric acid at ordinary atmospheric temperatures, but, on the contrary, he notes that the most reactive ones, amylenes and hexylenes, give amber-colored solutions in sulphuric acid. On standing these solutions give steadily increasing proportions of light, amber-colored, oily polymers, which form an upper supernatant, oily layer.

Formation of Aldehydes.

Oxidation to aldehydes and polymerization of these is considered by Smith and Cooke^{17a} to be the cause of the formation of gummy substances and resins from cracked gasoline. Moisture and light accelerate the conversion.

¹⁶ *J. Ind. Eng. Chem.* 1915, 7, 1029; note also U. S. Patents 1,318,060 and 1,318,061 of Oct. 7, 1919.

¹⁷ *Chem. Met. Eng.* 1921, 1024; note also Brooks and Humphrey, *J. Am. Chem. Soc.* 1918, 852; *J. S. C. I.* 1921, 446R.

^{17a} *Reports of Investigations* No. 2394, September, 1922, Bureau of Mines.

To study the effect of air, two samples of gasoline were heated for 100 hours in flasks with reflux condensers, both with water present. Through one of them a slow current of air was passed; through the other a slow current of hydrogen. The sample through which the air was passed deposited 3.24 per cent of gum, and on evaporation at the end of the run gave 3.39 per cent of gum in addition—a total of 6.63 per cent. The sample through which hydrogen was passed, which was heated the same length of time under the same conditions, deposited only 0.17 per cent of gum and on evaporation showed only 0.51 per cent, a total of 0.68 per cent, about 10 per cent as much as in the sample through which air was passed. The amount of unsaturated hydrocarbons present in a sample of gasoline is usually estimated by determining the solubility of the gasoline in concentrated sulphuric acid. In order to ascertain if the amount of gum that could be made from a sample of gasoline had any relation to the "unsaturation," as so determined, a sample of the above gasoline was heated for 100 hours in the presence of water, with a current of air passing through it. At the end of this time the sample was decanted from the separated gum and then distilled in a current of steam so that any gum that had formed in the gasoline itself could be recovered. The distillate from the steam distillation was again oxidized in the presence of water for 100 hours, and this process was repeated until more than 7 per cent of gum had been obtained. The "unsaturation" of the original gasoline was 18 per cent; the "unsaturation" of the gasoline from which 7 per cent of gum had been made was 17 per cent. This result, according to Smith and Cooke, indicates that there can be no quantitative relation between the so-called "unsaturation," as measured by solubility in sulphuric acid, and the amount of gum that can be made. To check this point, two samples of gasoline were prepared. One sample was a distillate boiling between 140° and 170° C. (284° and 338° F.). This product was thoroughly treated with acid and alkali, and after being thoroughly washed it was steam distilled over caustic potash. It was an absolutely water-white product with an entirely sweet odor. The "unsaturation" was less than 1 per cent. The second sample was prepared by steam stilling cracked gasoline over caustic potash. This sample had an "unsaturation" of 18 per cent. Each of these samples was oxidized by heating under a reflux condenser on a steam bath with a gentle current of air for 300 hours. The cracked gasoline which originally had 18 per cent of "unsaturation" developed 4.14 per cent of gum, and the "unsaturation" of the residual gasoline was still 18 per cent. The saturated gasoline developed 0.97 per cent of gum, and in the process developed an "unsaturation" of 8 per cent. During the tests made by Smith and Cooke it was noted that the gum as first formed was soft and sticky. As it was heated it became harder, and on prolonged drying it became a hard brittle resin. This hard resin was only partly soluble in acetone, whereas the soft gum was entirely soluble.

At first Smith and Cooke thought that phenol aldehyde resins were formed but the absence of phenols and further investigations on the behavior of aldehydes led them to the conclusion that aldehydes alone were responsible for the resinification. A water extract of the gasoline undergoing investigation gave a gummy residue on evaporation. It was found that the gum-forming tendency was reduced by washing with water. In one case sodium bisulphite yielded a crystalline substance characteristic of valeric aldehyde. On the addition of phenol to an aqueous extract of gasoline, in the presence of a small amount of sodium acetate serving as a catalyst, a resinous substance was formed.

Smith and Cooke note that acid treatment reduces the amount of unsaturation in gasoline and probably changes to some extent the character of the unsaturated bodies present. While there is no direct relation between the percentage of unsaturation and gum-formation

there is undoubtedly an indirect connection. A highly unsaturated gasoline can be oxidized more easily than a saturated sample, therefore the conclusion is reached by Smith and Cooke that aldehydes are formed in gasoline largely by the oxidation of olefines. From the data presented there is no evidence to determine whether the simple olefines or the diolefines are mainly responsible for the change, but observations made by others indicate a greater susceptibility to oxidation on the part of diolefines.

Dunham's Process.

Dunham¹⁸ proposes to utilize these bodies, objectionable in gasoline, to derive a resin.

He secures a resinous product by passing a mixture of hydrocarbon vapors or gases containing di-enes, such as isoprene or its homologues, in amounts of 5-10 per cent, through a heated container holding bauxite or fuller's earth or animal or vegetable charcoal or porous clay maintained at approximately 200° C. to effect polymerization with the formation of a resinous product. While molten, this flows down through the material and is drawn off. It solidifies to a brittle mass, somewhat resembling the darker varieties of colophony in appearance, melting at 75-100° C. and beginning to vaporize about 270° C. The resin is soluble in alcohol, readily soluble in hot and cold benzol and in acetone and somewhat soluble in ether. About half of the product is soluble in gasoline. It is suitable for the manufacture of varnish. The vapors used for this treatment may be obtained by cracking kerosene or other mineral oil under high pressure. The unchanged gases passing through the polymerization zone may be recharged with di-enes and recirculated through the heated material. A nearly quantitative conversion of the di-enes to resinous products is effected. The resin apparently has the composition $(C_{10}H_{16})_n$. It is suitable for use in insulating compositions and may be vulcanized with sulphur. A mixture of isoprene with gasoline may also be used as starting material but the cracked petroleum products are preferred for economy.

Process of Leslie and Barbre.

The refining of gasoline, naphtha, burning, lubricating and other oils and simultaneous production of a commercial synthetic resin by the action of finely divided porous substances at an elevated temperature is described by Leslie and Barbre.¹⁹

Oil is charged into a digester provided with reflux and ordinary condensers and the polymerizing agent is then added. The latter may be fuller's earth, kieselguhr, clay, charcoal, powdered coke or the like, in admixture with a substance of alkaline tendency such as calcium carbonate or other weak acid salts of any of the alkali or alkaline earth metals. Alternate refluxing and distillation is employed, that is the charge is first boiled under reflux with subsequent elimination of some refined distillate. Refluxing is next employed at a temperature which is higher than in the case of the initial treatment under reflux on account of the elimination of the more volatile fractions. Alternate refluxing and distilling is continued until the polymerization of unsaturated hydrocarbons, etc., has proceeded to the desired stage. The final product is given a steam distillation to eliminate heavy oils, leaving a residue which on cooling exhibits resinous properties.²⁰

¹⁸U. S. Pat. 1,324,649, Dec. 9, 1910; J. S. C. I. 1920, 164A; British Pat. 138,046, 1919.

¹⁹U. S. Pat. 1,337,523, Apr. 20, 1920.

²⁰Ellis and Meigs, "Gasoline and Other Motor Fuels," New York, 1921, 120.

Oxidation of Paraffin Oil.

Liquid paraffin of the German Pharmacopœia, when oxidized in sulphuric acid with potassium permanganate, yields a soft resin. If first oxidized in alkaline solution by permanganate and further oxidized in acid solution, a brittle resin softening at 75° C. is obtained. The resin is partly soluble in hot caustic potash solution, is easily soluble in benzol, chloroform, turpentine, ether, alcohol and acetone, and is soluble with difficulty in carbon tetrachloride, methyl alcohol and heavy benzine.²¹ Chlorine resinifies paraffin oil, the addition of potassium bichromate favoring the formation of solid products. If bichromate and hydrochloric acid are used, the reaction is liable to become violent and requires careful attention. By heating 2 parts of liquid paraffin oil with 2.5 parts of nitric acid sp. gr. 1.486 for 10 hours at 90–100° C., adding 0.5 part nitric acid and heating 2 hours longer, solids were obtained, which when dissolved in 15 per cent caustic potash solution and acidified with hydrochloric acid, gave a 75 per cent yield of resinous brown fatty acids. Yellow vaseline and paraffin wax also were examined. From the latter a product of ointment-like consistency was derived. Vaseline yielded a solid and an ointment-like resin, the latter containing no acid constituents.^{21a}

Chlorinated Paraffin.

Paraffin, ceresin, montan wax and petroleum oil can be chlorinated to a high degree by dissolving in carbon tetrachloride and introducing chlorine for a protracted period. The temperature may rise during the early stages of the reaction and after the temperature has fallen the introduction of chlorine should be continued for some time. In this way a transparent solid body is obtained from paraffin by the introduction of 70 per cent of chlorine. Highly chlorinated paraffin is very resistant to acids and alkalis. It is not attacked by boiling nitric acid of 65 per cent strength, concentrated hydrochloric acid or 10 per cent aqueous caustic soda solution. Chlorinated ozokerite is scarcely attacked by fuming nitric acid at 300° C. under pressure. In spite of this resistance to strong reagents, there exists the tendency of chlorinated products of this character to split off hydrochloric acid on long standing. Chlorine is not so firmly united as is the case with, for example, that present in the chlor naphthalenes (halowax).²²

Chlorinated Oils.

Blakeman²³ treats drying oils, paraffin wax, naphthalene and various other raw materials with chlorine and introduces the chlorinated product into paints. Asphaltic oils, fish oils, waxes and coal tar, all

²¹ Langer, Chem. Z. 1921, 45, 466; Chem. Abs. 1921, 2717.

^{21a} Vanadium oxide and sulphide are reported to have a thickening and resinifying action on certain petroleum oils when heated with the latter exposed to the air at a temperature of about 100° C.

²² C. F. Boehringer & Soehne, German Pats. 256,856, Nov. 19, 1910; 258,156, Dec. 28, 1911.

²³ Blakeman, U. S. Pat. 989,225-6-7, April 11, 1921.

chlorinated to a greater or lesser degree are employed by Ellis²⁴ in the production of flameproof insulation. A mixture of chlorinated asphaltum and chlorinated vegetable oil, the latter serving as a toughening agent, is employed by Wickenden²⁵ in paints and varnishes. For example 10 to 20 per cent of cottonseed oil and petroleum asphaltum or pitch of melting point 120° C. are mixed and chlorinated in a solution of carbon tetrachloride until the chlorination is quite complete. The solvent afterwards may be removed by distillation.

Dechlorination Process.

Bielouss²⁶ and Gardner^{26a} chlorinate petroleum and then dechlorinate the product by heating to 220-240° C. to obtain a drying oil. If the temperature during dechlorination rises above 250° C. resinous and asphaltic substances are formed.

Viscid resinous condensation products are produced from heavy hydrocarbons by successive halogenation and de-halogenation, followed by evaporation, or from heavy petroleum oil by chlorination, with subsequent washing, and treatment with Devarda's alloy.²⁷ On distillation the resinous products give a residue of pitch, while the distillate can again be submitted to treatment. The residue is suitable for brewer's pitch.²⁸

Formolite Resins.

Some of the cyclic non-benzenoid hydrocarbons react with formaldehyde in the presence of concentrated sulphuric acid or anhydrous aluminum chloride forming resinous condensation products.

This procedure has been termed the formolite test or reaction and has been advocated by Nastjukow²⁹ as a means of quantitative determination of these cyclic hydrocarbons. Cyclohexane, anhydrous aluminum chloride and trioxymethylene react to yield a condensation product of a resinous nature. The test carried out in the manner advocated by Nastjukow involves mixing the petroleum fraction with an equal volume of concentrated sulphuric acid, the latter being added in small portions and a half volume of aqueous formaldehyde solution is then added with agitation. A precipitate is formed which after washing with petroleum ether and ammonia water is a brown powder.³⁰

²⁴ U. S. Pats. 1,246,809 and 1,246,810, Nov. 13, 1917; 1,248,638, Dec. 4, 1917.

²⁵ U. S. Pat. 1,398,084, Nov. 22, 1921.

²⁶ U. S. Pat. 1,384,423, July 12, 1921.

^{26a} U. S. Pat. 1,384,477, July 12, 1921.

²⁷ Devarda's Alloy is an alloy of aluminum with varying amounts of copper and zinc. One composition is aluminum 59 parts, copper 39 parts, zinc 2 parts.

²⁸ Rebs, German Pat. 343,466, Aug. 7, 1915; J. S. C. I. 1922, 41, 110A.

²⁹ Journ. russ. phys.-chem. Ges. 1904, 881 and 1915, 47, 46; Trudi Bakuer Techn. Ges. 1908, Nr. 5; Gurwitsch, Wissenschaftliche Grundlagen der Erdölbearbeitung 1913, 46; J. S. C. I., 1904, 1082.

³⁰ Some German chemists comprehend under the term "Formolite" all resins yielded by the action of formaldehyde on any substances capable of reacting with this aldehyde to form resinous bodies. The resinifying reactions of formaldehyde are so varied and the products so diverse, physically and chemically, that such a manner of classification is considered by the author to lead to much confusion.

Acetaldehyde and Methylal.

According to Herr³¹ acetaldehyde and methylal likewise form condensation products with the aromatic constituents (naphthenes) of petroleum oil and its distillates, in the presence of sulphuric acid.

One part by weight of the oil when dissolved in two parts of methylal and four parts of concentrated sulphuric acid introduced as a thin stream yields a product which is separated by pouring the liquid into water, neutralizing with ammonia, and filtering. If the liquid is kept cool during the reaction, the product obtained is soluble in chlorbenzol. If the liquid is allowed to become hot, and is finally heated on the water bath for half an hour, a larger yield is obtained of an insoluble product. A rapid rough comparative determination of the unsaturated constituents of an oil can be made by taking 2 cc. of the oil in a graduated stoppered cylinder, adding 4 cc. of methylal, dissolving in 10 cc. of light petroleum, adding 2 cc. of sulphuric acid and shaking for one minute. After standing for half an hour, the volume of the condensation product which has settled is read.

Stannic Chloride.

Anhydrous stannic chloride³² polymerizes the oxygenated bituminous bodies of petroleum. Only a very small quantity of the reagent is necessary in order to produce a bulky precipitate from a heavy crude distillate. The chloride acting directly upon tars, converts them into solid asphaltum or pitch-like products. Pine tar, for instance, is converted into a solid, lustrous, pitch-like body on treatment with 10 or 15 per cent of stannic chloride. The reaction is very vigorous and is accompanied with liberation of much heat.

Resinification of Mineral Oils.

Holde³³ gives the following results of experiments, on the behavior of mineral oils when exposed in thin layers to the air.³⁴

Samples spread out thickly were heated to 100° C. for about 7 hours daily, and gave the following results: Colorless, resin-free paraffin oil (from the lowest lubricating oil fractions) gradually volatilized by the end of 15 months without leaving any trace of resinous residue; the thicker "motor" oil from the higher fractions left a small solid residue, consisting partly of original resin and partly of oxidized hydrocarbons; a very thick Russian oil volatilized only slightly and resinified but little, especially when previously extracted by 75 per cent alcohol. On the other hand lubricating oils (Russian and Oelheim) containing residuum, resinified considerably, and the first-named, which contained the larger proportion of low-boiling fractions, volatilized more rapidly and left a larger residue than the other Russian oil referred to above.

Nature of Petroleum Resins.

The solid constituents of mineral oils, Marcusson³⁵ says, consist of two classes, hydrocarbons and compounds containing oxygen. The latter are composed of acids (in negligible amounts), resins, and asphaltic substances. The portion soluble in light benzene is the mineral oil resins which form a transition group between the hydrocarbons and

³¹ Chem. Z., 1910, 34, 893; J. S. C. I. 1910, 29, 1094.

³² Torossian, J. Ind. Eng. Chem. 1921, 13, 904.

³³ Mitt. K. t. Versuchsanst. Berlin. 14, (4), 229; J. S. C. I. 1897, 363.

³⁴ J. S. C. I. 1895, 894.

³⁵ Chem. Z. 1915, 39, 581, 613.

asphalts. Nitration showed that both the resins and asphalts are apparently poly-cyclic compounds. The first stage of oxidation of the hydrocarbons produces the resins and further oxidation results in asphaltene. The second step occurs slowly at ordinary temperature, rapidly and completely at 120° C., or by auto-oxidation of the saturated and unsaturated hydrocarbons, the latter usually being polymerized at the same time.

Marcusson³⁰ considers the petroleum resins of natural asphalts to be the first stage in the conversion of petroleum hydrocarbons into asphaltenes. He describes them as solid reddish brown to brownish black masses which melt below 100° C. They are soluble in petroleum spirit, chloroform, carbon disulphide and benzol and have a specific gravity which approximates 1. Sulphuric acid at 100° C. converts them into insoluble sulphur compounds while sulphuric acid and formaldehyde react with them to form sparingly soluble precipitates. He considers that the asphaltenes may be formed by the action of oxygen or sulphur on petroleum resins as well as by intra-molecular changes within the resins. He found when the resins were heated for some time at 120° C. that they lost their solubility in petroleum spirits, became deep black and were converted into asphaltenes.

Ruth and Asser³¹ describe a process for manufacturing materials resembling rubber or linoxyn which consists of treating a feebly alkaline solution of an alkali naphthenate with an aluminium or chromium solution until a salt of hexanaphthenecarboxylic acid (o-methyl-cyclopentanecarboxylic acid) begins to be precipitated; in this way the unpleasant odor of the naphthenates is removed. The naphthenates obtained, when heated to 170° C., yield very viscous solutions resembling solutions of rubber, while at 300° C. a horny mass is produced which gives mobile solutions in turpentine, pine oil, and solvent naphtha.³²

³⁰ Z. angew. Chem. 1916, 29, 346, 349; J. S. C. I. 1916, 1099.

³¹ J. S. C. I. 1921, 188A; German Pat. 327,913, Feb. 18, 1919.

³² The composition of artificial asphalts is discussed by Marcusson, Mitt. K. Materialpruf., 1918, 36, 209; J. S. C. I. 1916, 1099; 1918, 403A; 1919, 453A. For removal of resin-forming hydrocarbons from mineral oil see Rebs, German Pat. 348,089, April 24, 1917; J. S. C. I. 1922, 41, 321A. Products obtained in refining Oklahoma petroleum. Thiele, Chem. Ztg. 1913, 37, 841; J. S. C. I. 1913, 781. For methods of separating resins from mineral oils, residuum and acid sludge by solvents, see Diamand, German Pat. 176,408, July 12, 1904; and 173,616, July 26, 1904; Chem. Abs. 1907, 1350; J. S. C. I. 1907, 87. Daeschner, Rev. prod. chim. 4, (20), 309; J. S. C. I. 1902, 168 and 765; British Pat. 10,663, 1901; Singer, British Pat. 109,270, 1917; Chem. Abs. 1918, 93. An asphalt-like product is obtained by washing acid sludge with gasoline to remove oils remaining in the sludge and with water to remove sulphuric acid, Landsberg, U. S. Pat. 1,211,721; Chem. Abs. 1917, 11, 1039. Acid resin obtained in refining petroleum, after removal of free acid, is dried and agitated at 120-125° C. with concentrated sulphuric acid, Harburger, Chem. Werke Schon und Co., German Pat. 333,169, Dec. 11, 1918; J. S. C. I. 1921, 339A. Acid tar, note Wass, J. S. C. I. 1888, 683; British Pat. 13,885, October 13, 1887. Hardening tar, Trillich, J. S. C. I. 1908, 974; German Pat. 200,524, March 26, 1907. Bernstrop and van Ledden Hulsebosch, J. S. C. I. 1899, 361; British Pat. 8462, April 9, 1898, state that the solidification of petroleum residues is effected by intimately rubbing together for a prolonged period a mixture of them and resin with slaked lime and water, until there is produced a tough mass that will harden when left to itself. This can then be molded by pressure into a firm body. Asphalts in petroleum refining, note Forward and Davidson, J. S. C. I. 1899, 128; British Pat. 20,879, Oct. 4, 1898. Montupet, J. S. C. I. 1903, 1289; French Pat. 332,772, June 4, 1903, produced a synthetic asphalt by mixing finely powdered calcium carbonate with a hydrocarbon base, and heating the mixture for some time at 140° to 150° C. in a rotatable vessel. Soriano, J. S. C. I. 1903, 1196; J. S. C. I.

Pitch Resin.

The distillation of coal tar to obtain anthracene and carbazol yields a residue known as hard pitch. When the latter is heated to convert it into coke, about 2 per cent of an orange-colored resin is collected as a sublimate or distillate. This product is known as pitch resin. It is a sticky mass which darkens on exposure to air.

The crude resin, according to Bailey and Boettner³⁸ contains dark-colored oily impurities and may be purified by dissolving in toluol and allowing separation to take place. 1000 parts of crude resin to 120 parts of toluol are incorporated by heating, then slowly cooled. Upon cooling, the solution contains

1904, 55, mixed a bitumen composition with an alkali earth compound. Acid sludge, Zaloziecki, Chem. Rev. Petrol. Harz.-Ind. 5, (2) 27; J. S. C. I. 1898, 340. To convert acid tar from petroleum into a product resembling well purified soft bitumen, the tar is kneaded with an amount of iron filings or borings more than sufficient to combine with the sulphuric acid present, Thompson, Rave, J. S. C. I. 1888, 303 and 377; 1889, 112; British Pat. 607, 1888. According to Burstin, Petroleum Z. 1921, 17, 1109, dilute caustic alkali first extracts naphthenic acids from mineral oils, further extraction yielding resins. Oxidizing petroleum residues, note Grey, J. S. C. I. 1898, 1137; British Pat. 18,302, Aug. 25, 1898. Adiasiewitsch, Zap. imp. russk. techn. obschtsch. 29, 93; J. S. C. I. 1896, 346, produced resinous material from lubricating oil residuum by blowing with "de-oxygenated" air at 150-200° C. and subjecting the material to a simultaneous discharge of electricity. Note also Koundjy, Bull. de la Soc. d'encouragement pour l'industrie nationale, 94, 1116; J. S. C. I. 1896, 533. Burkley, U. S. Pat. 1,300,520, June 10, 1919, subjects a mixture of gilsonite, 5 parts, and cylinder oil, 6 parts, to air-blowing at 175-255° C. for about 3 hours producing a tough, plastic material with a dull lustre. Schmidt, British Pat. 142,507; Kunststoffe, 1921, 22, treats paraffin wax to produce resin acids and fatty acids by exposing the wax at a temperature 100-200° C. for a considerable period of time to a blast of air or oxygen. Hermes, J. S. C. I. 1902, 1326; British Pat. 10,423, May 6, 1902, makes a mixture of 11 parts, by weight, of tar and 2 parts of resin, which is melted, and after the addition of 1 part of sulphur mixture is heated beyond the melting point of the latter ingredient. Combination occurs, and when the mass has become thick and brown, 11 parts of powdered lime are added. The resulting product forms a brown transparent resinous mass, insoluble in water. See also Alexander, J. S. C. I. 1899, 1021; British Pat. 24,629 and 24,630, Nov. 22, 1898. An elastic insulating mass is made by heating stearine pitch with sulphur at about 155° C., Marcusson, Mitt. k. Materialpruf. 1918, 36, 209; J. S. C. I. 1916, 1099; 1918, 403A; 1919, 453A. Note also British Pat. 3045, 1894; J. S. C. I. 1894, 531. Landsberg, Chem. Abs. 1914, 8, 3235; British Pat. 8069, April 5, 1913, treats oils, obtained by dry distillation of acid sludge compounds, with sulphur and sulphur dichloride to obtain an insoluble sulphur product. The soluble bitumen of coal tar and coal tar pitch, according to Marcusson, Z. angew. Chem. 1918, 31, 113, contains, in addition to phenols and hydrocarbons, three distinct tar resins, respectively soluble in benzol, chloroform and pyridine. Harburger Chem. Werke Schön & Co., and Daitz, J. S. C. I. 1921, 339A and 651A, make a hard asphalt from soft pitch by heating the latter with water and mineral matter. Reif, German Pat. 332,941, Jan. 3, 1920; J. S. C. I. 1921, 427A, causes a tar fog to circulate and impinge on the periphery of a moving annular cloud of filling material so as to envelop and penetrate the latter. In order to obtain a product possessing hardness, elasticity, and resistance to heat, the tar, or a mixture of tar and oil, is first oxidized or treated with a halogen or sulphur and then incorporated with the filling material. See also Wardell, U. S. Pat. 1,385,511, July 26, 1921.

³⁸ U. S. Pat. 1,355,103, Oct. 5, 1920.

solid masses. These are separated by filtration and washed with toluol, yielding a yellow powder which does not darken on exposure to air and consists largely of hydrocarbons melting at about 290° C. and over. This yellow material amounts to about 8 per cent of the original resin. The filtrate is distilled to remove the solvent and the residue is submitted to distillation in vacuo. With an absolute pressure of 8 mm. oils and greases are obtained up to 275° C. Above this temperature to about 400° C. red resins of varying hardness distil. The hardest species of these resins melt between 75° and 100° C. and are not discolored by air and light. The resins are soluble in benzol, carbon tetrachloride, linseed oil and partially soluble in methyl and ethyl alcohol.

According to Weiss^{38a} vulcanized rubber compositions of light color are formed by incorporating with the rubber mixture prior to vulcanization, a light-colored semi-solid or solid bitumen such as may be obtained by the destructive distillation of coal-tar pitch, and then subjecting the mixture to vulcanization.

Stearine pitches.

All fatty acid pitches have the property of becoming insoluble and less fusible on exposure to the weather for a protracted period and the change takes place quickly in the presence of air at a temperature of 250-350° C.³⁹ Blowing with heated air raises the melting point and tends to form insoluble compounds.⁴⁰ Insoluble and infusible substances are formed by heating with sulphur.⁴¹

^{38a} U. S. Pat. 1,282,505, Oct. 22, 1918; Chem. Abs. 1919, 270.

³⁹ Note Vogelsang, German Pat. 217,026, 1905; Connolly, British Pat. 3345, 1906; Böerche, U. S. Pat. 842,615, Jan. 29, 1907.

⁴⁰ Schreiber, German Pat. 208,378, Sept. 13, 1905.

⁴¹ Griscom, U. S. Pats. 529,727, 529,728, 529,729, 529,730, Nov. 27, 1894; Bäärnhjelm and Jernander, German Pat. 77,810; Malchow, German Pat. 225,911.

Chapter 6.

The Resinous Condensation Products of Phenols and Aldehydes.

HISTORICAL

The products obtained by the condensation of phenols with aldehydes form a group comprising an enormous number of species. Some of these are crystalline, others are resinous bodies. The present chapter is concerned with the resinous substances only and includes an historical sketch of the early investigations on these resins, and the development work which resulted in phenol-aldehyde resinous condensation products achieving a high pinnacle of commercial success.

Condensation of Salicylates.

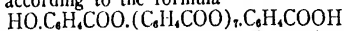
An insoluble resinous body was obtained by Gerhardt¹ as early as 1853 by the dehydration of sodium salicylate through the action of phosphorus oxy-chloride. The course of the reaction is indicated as follows: $2(\text{C}_7\text{H}_6\text{O}_3) \rightarrow \text{C}_{14}\text{H}_{10}\text{O}_6 + \text{H}_2\text{O}$. Gerhardt observes that the resin is acted upon by aqueous caustic potash. Schroder, Prinzhorn and Kraut,² in 1869, found the dehydration of sodium salicylate with phosphorus oxychloride produced a resin which was insoluble in water, alcohol or ether and which when treated with caustic potash could be hydrolyzed yielding salicylic acid.³ Velden⁴ showed that salicylic acid in the presence of sodium amalgam and acid would form oxybenzyl alcohol by reduction and then by dehydration become a saliretin body. Baekeland⁵ also has shown resinification of this character to occur when salicylic acid is reduced at the cathode by electrolysis.

A white amorphous powder was obtained by Doebner⁶ on condensing salicylic acid with gallic acid. It has been recommended as an antiseptic.

¹ Ann. der Chemie, 1853, 87, 159.

² Ann. der Chemie, 1869, 150, 1.

³ An octo- or nono-salicylosalicylic acid may be formed. The probable linking of the chain is according to the formula



See Beilstein and Seelheim, Ann. 1861, 117, 87. Also Redman, Weith and Brock, J. Ind. Eng. Chem. 1914, 6, 3.

⁴ Jahresbericht, 1877, 5, 37.

⁵ J. Ind. Eng. Chem. 1912, 4, 737.

⁶ Centr. Blatt. 1898, I, 229; German Pat. 94,281.

Baeyer's Work.

Any discussion of the resinous condensation products of aldehydes and phenols, lacking reference to the work of Baeyer in 1872, would be incomplete. At this early date Baeyer⁷ announced the reaction between phenols and aldehydes to be a general one. He noticed that oil of bitter almonds (benzaldehyde) united with pyrogalllic acid on heating in a manner resembling phthalic acid. A colorless resinous substance associated with a red oxidation product was obtained. The colorless resin was obtained immediately in the cold when pyrogalllic acid in hydrochloric acid was mixed with oil of bitter almonds well agitated with hydrochloric acid.

Resorcin and oil of bitter almonds react in like manner when concentrated sulphuric acid is added gradually to such a mixture. Thickening occurs and after purification a red resin is obtained. The resin dissolves in concentrated sulphuric acid, forming a water-soluble substance.

Acetaldehyde and Phenol.

When acetaldehyde was added to a mixture of concentrated sulphuric acid and phenol Baeyer found the mixture to thicken and on the addition of water to yield a white sticky substance. This was soluble in caustic potash affording a violet colored solution. Aldehyde ammonia dissolved in hydrochloric acid and admixed with pyrogalllic acid in concentrated hydrochloric acid yielded a white precipitate which was soft and was easily soluble in hot water. By heating the aldehyde with pyrogalllic and hydrochloric acids a red substance was obtained. Chloral acted similarly to aldehyde.

Michael's Investigations.

The reaction between benzaldehyde and phenols was studied by Michael,⁸ who obtained various resinous bodies. Phenol and benzaldehyde in alcoholic solution, in the presence of a trace of hydrochloric acid, did not react in the cold but on heating for several hours a resin was obtained. Orcin, resorcin and pyrogallol reacted with benzaldehyde in the cold in the presence of hydrochloric acid. An evolution of heat was observed. Salicylaldehyde also reacts with phenol. Resorcin and benzaldehyde heated in a closed tube to 200° C. form a resin but heating in open vessels does not bring about a reaction. In the presence of acids the union takes place far more readily. A trace of hydrochloric acid causes the formation of a white amorphous compound. Water may be used in place of alcohol as a diluent. On heating to boiling the aldehyde gradually unites with the resorcin and is completely converted into a resin. To obtain the resin in pure form Michael treated a solution of equal parts aldehyde and resorcin in 3 parts of alcohol with a minute amount of hydrochloric acid and after the reaction was complete allowed the solution to cool and filtered from crystalline material. The filtrate was poured into water and a white resinous mass precipitated which was extracted several times with a large quantity of cold water, redissolved in a small amount of alcohol and reprecipitated by pouring into water. All attempts to obtain this body in a crystalline form were without success. The white material when it contained con-

⁷ Ber. 1872, 5, 25, 280 and 1094.

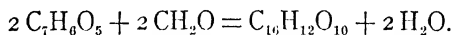
⁸ Am. Chem. J. 1883-1884, 5, 338.

siderable water remained unchanged on contact with the air but darkened when the water was removed. Before drying at 100° the resin is insoluble in boiling water but melts under it to a reddish mass. It is very soluble in alcohol, benzol, ether and glacial acetic acid. On exposure to the air it gradually takes up oxygen and is converted into a dark brown substance, decomposition taking place very rapidly when the resin is heated. The latter dissolves readily in alkalis and the solutions become discolored quickly on exposure to air. The dried resin is also soluble in alkalis. It melts with complete decomposition at a high temperature, somewhat above 330° C. Michael prepared an acetyl derivative as a white amorphous substance somewhat less soluble in alcohol and benzol than the parent resin. The acetyl compound was found insoluble in alkalis in the cold. Michael found the crystalline material formed in alcoholic solution during the preparation of the resin was due to the action of hydrochloric acid on the resin.* The activity of acids as catalysts varies with their strength, hydrochloric and sulphuric acid being most active. Phosphoric acid is somewhat less vigorous and organic acids such as acetic, formic, lactic and oxalic acids are much less active. Alkalis also were found to have a catalytic effect. Caustic soda, caustic potash and potassium carbonate likewise yielded resins of a similar character. In preparing the resins when employing alkaline catalysts it is necessary to keep the solution as much as possible from the air as oxidation takes place with darkening.

Trzciński⁹ treated 3 parts by weight of betanaphthol and 1.5 parts of benzaldehyde in 1.5 parts alcohol with 1 part of concentrated sulphuric acid and obtained a crystalline body but the same procedure applied to alphanaphthol yielded only resinous products.

Kleeberg's Researches.

By 1890 formaldehyde was a commercial preparation and at the instigation of Prof. Emil Fisher investigations were carried out by Kleeberg⁹ on the condensation products of formaldehyde with the phenols. Kleeberg refers to the work of Baeyer on aldehydes and to that by E. ter Meer¹⁰ on methylal and to certain condensation products of methylal and phenol which possessed a resinous character and were not further investigated. Kleeberg found that formaldehyde reacted energetically with phenol, resorcin and pyrogallol in the presence of strong hydrochloric acid to yield products which were insoluble in alkalis and were so difficult to purify that their composition could not be determined. With gallic acid a compound of a more definite character was produced. Kleeberg found present in the condensation products an acid having the formula $C_{16}H_{12}O_{10}$, apparently the result of a union of two molecules each of gallic acid and formaldehyde with the elimination of water.



Kleeberg's experiments with gallic acid consisted in treating a hot aqueous solution of 20 grams of the acid with 40 cc. of commercial formaldehyde solution, concentrated hydrochloric acid being added until the solution became turbid. On cooling a small amount of a brown resin and a larger quantity of a colorless amorphous substance

* Ber. 1884, 17, 499; note also Ber. 1883, 16, 2835.

⁹ Ann. d. Chem. 1891, 263, 283.

¹⁰ Ber. 1874, 7, 1200.

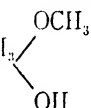
separated. The latter was particularly investigated by Kleeberg. It was found to be very difficultly soluble in all common solvents but easily soluble in fixed alkalies and aqueous ammonia. The condensation product proved to be an acid which in purified state was amorphous and colorless. On strong heating the substance carbonized without melting.

Formaldehyde and Phenol.

Kleeberg mixed 10 grams of phenol with 20 cc. of a 40 per cent aqueous formaldehyde solution and added concentrated hydrochloric acid with cooling. Reaction took place with evolution of considerable heat and a rose red viscous mass formed which solidified on cooling. The pulverized product was extracted by boiling with water and alkalies until the color had disappeared completely. The purified product was practically insoluble in all of the common solvents and in caustic alkali solutions. On heating it carbonized without melting. Analysis of various preparations made according to the foregoing gave no concordant results and Kleeberg concluded the substance was apparently a mixture of complex condensation products not possessing a phenol group.

Hosaeus¹¹ refers to investigations carried out by Tollens which were never published. The latter heated dilute formaldehyde solutions with phenol, resorcin, pyrogallol and phloroglucin, an addition of sulphuric or hydrochloric acid being made. In all cases resinous products separated which were either difficultly soluble or insoluble in all common solvents. Hosaeus treated betanaphthol with formaldehyde solution in the presence of acetic acid and obtained a crystalline product. Abel¹² also investigated the reaction between formaldehyde and naphthols and in general obtained crystalline substances. Menthol also yielded a crystalline body. Guaiacol when treated with formaldehyde and excess of guaiacol eliminated yielded a brittle yellowish mass which was soluble in alkalies.

An interesting research was carried out by Doebner¹³ on the synthesis of the acids of guaiac resin (guaiacum). The three acids found in this resin contain the complex radical $\text{CH}_3\text{CH}:(\text{CH}_3)\text{CH}<$ present

in tiglic aldehyde and also the guaiacol complex — C_6H_3  The

three acids of the natural resin appeared to differ essentially with respect to the number of hydroxyl groups present.

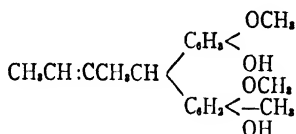
Doebner mixed 5 parts of tiglic aldehyde with 9 parts each of guaiacol and creosol diluted with 20 parts of glacial acetic acid. 2 parts of concentrated hydrochloric acid were added and the mixture was heated for 20 minutes on the water bath. The mixture was poured into about 250 parts of strong hydrochloric acid and heated for 15 minutes longer, then poured into cold water. A

¹¹ Ber. 1892, 25, 3212.

¹² Ber. 1892, 25, 3477.

¹³ Arch. der Pharm. 234, 610; Centr. Blatt. 1897, I, 167.

brown resin separated which was purified by distillation with steam. This removed the excess of guaiacol and creosol. The resin was further purified by dissolving in dilute caustic soda and precipitating with dilute acid. It was found to be soluble in alcohol. The purified resin was of a yellowish brown color apparently an isomer of guaiac resin. Its constitution is represented by the following formula:



By condensation of tiglic aldehyde with guaiacol and pyrogallol dimethyl ether a somewhat similar resin is obtained. Tiglic aldehyde and dimethyl pyrogallol yield a resin of the composition represented by the formula $\text{C}_{27}\text{H}_{30}\text{O}_6$. Doebner therefore draws the conclusion that the guaiac resin of the vegetable kingdom is a condensation product of phenols with aldehydes.

Litterschied and Thimme¹⁴ treated phenol and resorcin with monochlor-methylether $\text{CH}_3\text{O}.\text{CH}_2\text{Cl}$ and obtained insoluble bodies which they describe as having the appearance of porcelain and which they compare with the products obtained by Baecker¹⁵ from phenol, formaldehyde and hydrochloric acid.

Phenol Alcohol or Saligenin (*Ortho oxybenzylalcohol*).

As the phenol alcohol—saligenin—plays an important rôle in the formation of the resinous condensation products of phenol and formaldehyde a discussion of the chemistry of this compound finds appropriate place here. The simplest condensation product of phenol and formaldehyde is represented by saligenin.¹⁶ Being a crystalline substance it has been prepared in a pure state. Manasse used as a condensing agent various inorganic basic substances, namely caustic soda and caustic potash, potassium and sodium carbonate, quick lime, zinc and lead oxides, also zinc dust, sodium acetate and potassium cyanide. Lederer¹⁷ used milk of lime or baryta water.

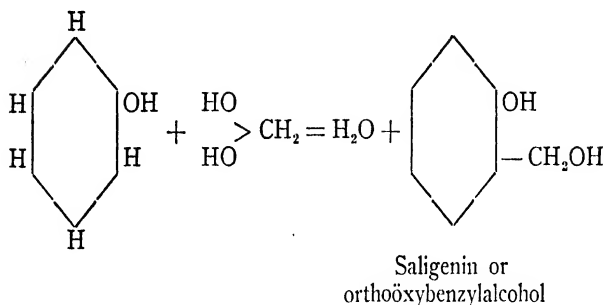
The phenol alcohol is conveniently made by dissolving phenol in somewhat more than an equivalent proportion of dilute caustic soda. A quantity of formaldehyde (40 per cent aqueous solution) in amount equivalent to one equivalent of the phenol used is added and the mixture is allowed to stand until the odor of formaldehyde has disappeared. Then the solution is neutralized with acetic acid and is extracted with ether which removes the phenol alcohols and the uncombined phenol. The latter may be removed by distillation with steam. Both the ortho and para oxybenzyl alcohol form. Manasse suggests the formation of these alcohols may take place in one of two ways. Thus the formaldehyde in alkaline solution may act as methylene glycol $\text{CH}_2(\text{OH})_2$ according to the following reaction:

¹⁴ Ann. 334, 49; Chem. Centr. 1904, II, 949.

¹⁵ Ber. 5, 1095.

¹⁶ Lederer, J. prakt. Chem. (2), 50, 224; Manasse, Ber. 1894, 2409; U. S. Pat., Manasse, 526,786, 1894; German Pat., Bayer, 85,588.

¹⁷ U. S. Pat. 563,975, July 14, 1896.



Or a simple aldol transformation may take place through formation of the alcohol group by the transfer of one hydrogen atom of the phenol.¹⁸

Similar oxy alcohols are formed from certain other phenols, thymol, for example, giving a crystalline product which on warming in the presence of mineral acids is resinified. On treating the alcohol with concentrated sulphuric acid and diluting with water a resin is precipitated.

Saliretin.

Piria prepared this resin by the action of dilute acids on saligenin.¹⁹ Saliretin may be prepared by warming 1 part of salicin with 10 parts of hydrochloric acid (sp. gr. 1.25) to 80° C. precipitating with water, dissolving the precipitate in moderately dilute alcohol and precipitating the solute with brine.²⁰ Saliretin is a yellowish powder soluble in alcohol and alkalis. The saliretin obtained from saligenin by Gerhardt²¹ by means of sulphuric acid corresponds to the formula $\text{C}_{28}\text{H}_{26}\text{O}_5$. That is, $4 \text{C}_7\text{H}_8\text{O}_2 \rightarrow 3 \text{H}_2\text{O}$; may be looked upon as the course of derivation of this product. Beilstein and Seelheim through heating of saligenin with acetic anhydride or with ethyl iodide obtained a saliretin of the composition $\text{C}_{56}\text{H}_{50}\text{O}_9$, that is the result of withdrawal of $7 \text{H}_2\text{O}$ from $8 \text{C}_7\text{H}_8\text{O}_2$.

Baekeland²² notes that saligenin or oxybenzyl alcohol is very easily disturbed by dehydration and that the removal of water brings about the formation of a resinous substance. The dehydration can occur by mere application of heat and is much hastened by strong acids and certain other chemical agents. Hence to

¹⁸ The separation of the two oxybenzyl alcohols is carried out by Manasse, U. S. Pat. 526,786, Oct. 2, 1894, as follows: An ether extract of the crude product is dried by means of sodium carbonate and the solution is then evaporated to dryness. A yellowish oil is obtained which crystallises after standing for a few days. The crystalline mass is treated with benzol at 50° C., which extracts the ortho oxybenzyl alcohol. From this solution the alcohol can be readily crystallised. Auwers and Daecke (Ber. 1900, 33, 3373) observe that paraoxybenzyl alcohol which has not been well purified may become resinous on standing.

¹⁹ Ann. 56, 37.

²⁰ Kraut Ann. 156, 124.

²¹ Ann. chim. phys. (3), 7, 215.

²² J. Ind. Eng. Chem. June, 1913.

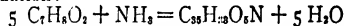
successfully prepare oxybenzyl alcohol low temperatures and general careful treatment are essential. The oxybenzyl alcohol produced in alkaline solution according to the method of Manasse is best isolated by careful neutralization by means of weak acids and extraction by solvents which separate it from the impurity of uncombined phenol. Unless such precautions are observed the reaction may get beyond control and resinous bodies be thus produced in large proportion. This is especially the case when strong acids are employed as condensing agents but even under such conditions Baekeland²⁸ has been able to establish the presence of noticeable quantities of oxybenzyl alcohol.

Salireton.

$C_{14}H_{12}O_3$. This substance is obtained by heating equal parts by weight of saligenin and glycerol for 8 hours in a sealed tube on water bath. The contents of the tube are diluted with water and the resin which is precipitated is boiled with water. Evidently the reaction progresses largely to a resinous body because the yield of salireton is given as $2\frac{1}{2}$ per cent on the saligenin.²⁹ When salireton is heated above $140^\circ C$, or even by protracted boiling with water, a resin is formed which is soluble in ether and alkalies.

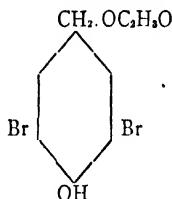
Saliretazine.

In 1894 Paal and Senninger³⁰ carried out some observations on the action of ammonia on saligenin (ortho-oxybenzyl alcohol), which are of especial interest in view of the development of commercial synthetic resins from phenol and formaldehyde condensation products. When saligenin is heated to 180 – $200^\circ C$ a basic condensation product is obtained in the form of a yellow amorphous body which is notable for its insolubility in acids, alkalies and various organic solvents. An analysis indicated the formula $C_{25}H_{21}O_2N$. The formation of this substance from saligenin and ammonia may be represented by the following equation:



Paal and Senninger tried many solvents including ether, alcohols, chloroform, acetone, glacial acetic acid, benzol, phenol, aniline, etc., without observing any indication of solubility. The substance was infusible and decomposed on heating above $300^\circ C$. This insoluble and infusible amorphous body is of interest in view of its bearing on Bakelite and similar infusible resinoid substances.

Auwers and Daecke³¹ prepared an acetyl compound of dibromoparaoxybenzyl alcohol (melting point 112 – $113^\circ C$).



When this product was treated with a small amount of caustic alkali and the solution acidified a reddish brown amorphous substance, melting at 240 – $250^\circ C$ with decomposition, was obtained. This substance was found to be insoluble in all common organic solvents. The substances formed more readily the more concentrated the solution and the longer the period of action of the alkali. A concentrated alkaline solution of the acetate in the course of a few minutes changed into a violet jelly which consisted entirely of the substance of high melting point.

²⁸ J. Ind. Eng. Chem. 1912, No. 10.

²⁹ Giacosa, J. pr. Chem. (2), 21, 221; Beilstein, 3rd Ed. II, 1109.

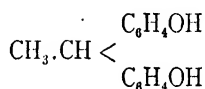
³⁰ Ber. 1894, 27, 1799.

³¹ Ber. 1900, 33, 3379.

Claus and Trainer's Researches.

In the course of some experiments on the production of acetals Claus and Trainer²⁷ observed the action of acetaldehyde on phenol in the presence of hydrochloric acid gas. In view of the violence of the reaction the following procedure was adopted. An equivalent of acetaldehyde to two equivalents of phenol were dissolved in ether and cooled while hydrochloric acid gas was passed through the mixture. Under these circumstances the reaction progressed quietly and on evaporation of the ether and the water produced by the reaction a reddish soft resinous mass remained. Removal of the uncombined phenol by treatment with steam yielded a hard and brittle resin. This product was insoluble in water, benzol and petroleum ether but dissolved easily in alcohol, ether, chloroform, acetone and glacial acetic acid. It was also soluble in a mixture of equal parts of benzol and ether. Efforts were made by Claus and Trainer to crystallize the resin from some of these solvents but in no case could a crystalline body be obtained. The resin dissolved easily in aqueous caustic alkali solutions and on acidification a white or rose colored precipitate was produced which retained inorganic salts very obstinately. The precipitated resin could not be obtained free from ash without very long extraction with hot water or solution in ether. This resinous material began to soften at about 100° C. and at 125° C. was viscous. Even at higher temperatures it did not become freely fluid.

An analysis indicated that one molecule of the aldehyde had united with two molecules of phenol with the elimination of one molecule of water. However instead of being an acetal the aldehyde had evidently joined the benzol nucleus through two hydrogen atoms to yield a compound which Claus and Trainer²⁸ named ethylidene diphenol having the formula



Claus and Trainer also determined the action of acetaldehyde and hydrochloric acid on the naphthols. Alphanaphthol behaved similarly to phenol in forming the ethylidenedialphanaphthol but the betanaphthol apparently formed an acetal. This difference in behavior recalls the work of Beckmann and Dehn on furfural resins (see Chapter 11), who found a very great difference in the character of the reaction between furfural and alpha and beta naphthol.

Molded Insulation by Smith's Process.

It is of interest to note that by the year 1900 phenol-aldehyde resins had been proposed for making electrical insulation. Smith²⁹ made a product in substitution for ebonite by diluting 2 volumes of paraldehyde with 1 volume of methylated spirit, adding 3 volumes of carbolic

²⁷ Ber. 1886, 19, 3004.

²⁸ See also Fabinyi, Ber. 11, 283.

²⁹ British Pat. 16,247, 1899; U. S. Pat. 643,012, Feb. 6, 1900.

acid (liquefied by 5 per cent of water) and finally to this mixture, in a closed container, gradually introducing 3 to 6 volumes of fusel oil or methylated spirit saturated with hydrochloric acid. The mixture was cooled to prevent the temperature rising above 80° F. (26.7° C.). The product was poured into greased molds and allowed to set. The shaped articles were removed from the molds and dried or baked at 212° F. (100° C.). When fusel oil was employed as the vehicle for adding hydrochloric acid the product was black. It was found to be resistant to most chemical reagents. Molded articles also were treated, either before or after drying, by gradually heating in molten paraffin wax or ozokerite to 100° C.

The maximum temperature of baking was reached during a period of 12 to 30 hours according to the thickness of the article. The temperature then was slowly reduced. This procedure is somewhat similar to certain methods subsequently employed in cold molding. Twice the quantity of pure acetaldehyde was used to replace paraldehyde; that is, 4 volumes of acetaldehyde to 3 volumes of liquefied phenol.

Formaldehyde.

Polymerized formaldehyde dissolved in fusel oil, saturated with hydrochloric acid or sulphur dioxide, also was recommended by Smith. The polymerized formaldehyde 1 part, was mixed with about 5 parts of the acidified fusel oil. Phenol crystals were introduced in an amount sufficient to add 50 per cent to the volume of the mixture. The composition set rapidly and could be shaped or fashioned in a manner similar to that employed with the paraldehyde composition. To any of these compositions 5 to 10 per cent of natural resins could be added, this being done before admixing the gas-saturated fusel oil or methylated spirit. By slightly reducing the proportion of the gas-saturated alcohol the composition was obtained in a plastic condition capable of being pressed into various forms. Asbestos was used as a filler. The resin is stated to be insoluble³⁰ in glacial acetic acid, chloroform, ether and alcohol.

Acetaldehyde and Resorcin.

Equal parts of these substances dissolved in 3 parts alcohol and slightly acidified with hydrochloric acid solidified on heating at 100° C. to a gelatinous mass, insoluble in the usual solvents.³¹

Blumer's Researches.

In the early part of 1900 a number of investigators were engaged in the study of the resinous condensation products of phenol and formaldehyde. Blumer³² sought to obtain a substitute for shellac by carrying out the condensation in the presence of an organic oxy-acid, tartaric acid being well adapted as a condensing agent. He recom-

³⁰ German Pat. 112,685, Oct. 10, 1899.

³¹ Michael and Comey, *Am. Chem. J.* 1883-1884, 5, 349.

³² British Pat. 12,880, 1902.

mended the following procedure: 135 parts by weight of tartaric acid are mixed with 150 parts of a 40 per cent solution of formaldehyde in a spacious jacketed vessel lined with lead. The acid is completely dissolved by heating gently and then 195 parts of commercially pure carbolic acid are introduced. Gentle heat is applied until reaction begins and from that time on the heat of the reaction serves to keep the contents of the vessel in ebullition for a period of about 10 minutes. The crude resin is found floating on the surface as an oily mass. This is placed in hot water and is boiled, ammonia being added. The treatment serves to eliminate the small quantity of phenol and formaldehyde present. When poured into cold water the resin at once solidifies to a white mass. Two different samples of this phenol resin gave closely agreeing results when subjected to elementary analysis. The substance most nearly corresponding to the elementary analysis would have the formula $C_{21}H_{20}O_4$.

Alphanaphthol.

The condensation of alphanaphthol is carried out by mixing 155 parts by weight of tartaric acid with 150 parts of aqueous formaldehyde, adding 290 parts of alphanaphthol and permitting combination to take place. The reaction progresses violently and the product is a red resin which sets very quickly to a hard mass. As the resin does not melt in hot water it cannot be purified as is the case with the phenol resin, hence Blumer recommends that the resin be pulverized for purification purposes. The resins obtained by Blumer are stated to be suitable for the manufacture of varnishes or polishes because they are readily soluble in various solvents such as alcohol, ether and oil of turpentine. Coatings obtained by the application of these solutions possess a good lustre and may be washed with soap or soda without impairment.

Another worker in the early part of 1900 was Luft.⁸³ He likewise used an acid catalyst or condensing agent, recommending sulphuric, hydrochloric and oxalic acids. For example he suggests mixing equal parts of phenol and a 40 per cent formaldehyde solution with sulphuric acid of 16-17° B., from 40 to 80 per cent of the acid being employed. The mixture is heated in a vessel equipped with a reflux condenser. Violent reaction takes place and a white viscous mass is obtained which settles. This is collected, washed and dried. In the fresh condition the resin is plastic but when dried it ultimately becomes brittle. The resin is not inflammable and is neither attacked by hot concentrated mineral acids nor alkalis. This property Luft remarks would make it suitable for preparing containers for acids, alkalis and other chemicals were it not for the brittleness of the material. Luft suggests addition of other substances such as camphor, rubber, glycerol or even alcohol, all of which he states prevent hardening of the mass.

Hot Pressing.

Luft also remarks that mechanical operations are not without influence on the properties of the resin. He states a harder and very elastic mass is obtained if the resinous material is pressed in slightly warmed molds.

⁸³ U. S. Pat. 735,278, Aug. 4, 1903.

Transparent Products.

To render the resin transparent it should be boiled (after previous washing with water) while in a viscous condition in the presence of a neutralizing agent, an alkaline carbonate being suitable. The resin is then washed and dissolved in a mixture of formaldehyde and glycerol. The solution is thickened by boiling and then is poured into molds and dried at a temperature of about 50° C. Acetone or alcohol may also be employed as solvents. Such solutions with or without the addition of coloring agents may be employed to obtain waterproof coatings on fabrics or leather. Luft also suggests drawing out the material into threads for the purpose of making carbon filaments for incandescent lamps.

Insulation.

As the resin is a non-conductor of electricity Luft observes that it may be employed for insulating purposes and also used as a substitute for celluloid. He states it may be employed in the manufacture of molded articles such as billiard balls, buttons and handles. Also it may be employed as an imitation amber, tortoise shell, meerschäum, vulcanite and coral. It may be used in making a species of linoleum.

Baekeland³⁴ prepared Luft's product and found it relatively brittle, very much less tough and flexible than celluloid. It does not melt if heated although softening considerably. Acetone swells it and appropriate solvents can extract free camphor and glycerol. In a controversy with Baekeland, Redman³⁵ discusses the Luft process. Redman states that the two steps which resulted in the production of Bakelite consisted in adding the basic condensing agent in certain proportions at the beginning of the reaction in place of adding the basic condensing agent after the reaction had proceeded for a short time in an acid solution in accordance with the Luft process, and in the use of increased heat and counter-pressure where it was necessary to prevent the escape of gases. Redman observes that Luft used an acid condensing agent at the beginning of the reaction then washed out the acid completely and added a basic condensing agent. He considers that Baekeland deviates from Luft's process in one step only, namely, that Luft added an acid at the beginning of the reaction and later washed out the acid and added a basic condensing agent while Baekeland adds the basic condensing agent at the beginning of the reaction. Replying to this Baekeland states³⁶ that the Luft process involving condensation with strong acids tends to give products of the permanently fusible or Novolak type; or by increasing considerably the amount of formaldehyde produces infusible resins contaminated with products of the Novolak type so as not to be suitable for technical purposes. He says if Luft

³⁴ J. Ind. Eng. Chem. 1909, 151.

³⁵ Redman, Weith and Brock, J. Ind. Eng. Chem. 1916, 473.

³⁶ J. Ind. Eng. Chem. 1916, 568.

recommended an alkali or alkali carbonate after the condensation with strong acids had taken place this was done simply in order to neutralize any remaining amounts of acids which otherwise are difficult to wash out of the mass.

A method of preserving wood developed by Bevier³⁷ consisted in impregnation at 150°-300° F. (66°-149° C.) and at a pressure of 100-400 lbs., with a mixture of creosote, formaldehyde and resin. This treatment is followed by a hardening process which may consist in forcing milk of lime or resinate of lime into the wood.

The next worker in this field was Story.³⁸ The process which he employed consisted in submitting phenols to the action of aqueous formaldehyde at a high temperature for a number of hours until a viscous product was obtained. This could be cast in molds and finally hardened by heating at a temperature below 100° C. 50 parts of commercial carbolic acid (95 per cent) to 30 parts of 40 per cent formaldehyde solution was recommended by Story. The vessel employed for heating was provided with a reflux condenser. At the end of about 4½ hours heating at 100° C. and with strong agitation the entire time the solution becomes cloudy. The heating is continued usually for a period of about 8 hours giving a product of somewhat creamy appearance.

Drying.

This product is transferred to an open vessel and concentrated rapidly, the temperature being raised above 100° in order to drive off as much water as possible. The product should now become clear especially if the preliminary boiling has not been carried on for too long a period. Gradually the product increases in viscosity and the temperature should be lowered below 100° after a time. Eventually a solid substance is obtained. This is hard, tough and transparent and is a good insulator of electricity. Opaque products are obtained when the preliminary boiling is continued for a longer time. A similar result also may be obtained if the concentration is conducted at a temperature below 100° C.

Molded Articles.

When shaped articles are desired the product in liquid form is poured into heated molds and these are placed in a drying oven at about 80° C. and solidification occurs. The mass shrinks sufficiently in drying to allow the article to be withdrawn from the mold. When a very light colored product is desired it is best, according to Story, that air and light should be excluded. The addition of small quantities of

³⁷ J. S. C. I. 1900, 827; British Patent 9989, 1900.

³⁸ British Pat. 8875, 1905.

fatty oils such as castor, almond, olive or rape oil is conducive to opacity. When air is excluded during the boiling operation and fatty oil is added a white substance which Story states has the appearance of ivory or bone will be obtained. The plastic material may be colored by pigments or dyes. A black product resembling ebonite is obtained by the addition of pitch, lamp-black, asphaltum or aniline black.

Varnish.

While the product is still in a viscous state it may be dissolved in alcohol, acetone or benzol and the solution is adapted for use as a varnish. If the solution is not too concentrated the coating will dry to a hard surface by mere exposure to the air. The material also may be heated to harden the resin and remove all trace of solvent. Such a varnish may be used for waterproofing paper and fabrics or may be employed as a vehicle in the preparation of paints.

Insoluble Resin.

Once the resin has become hard and dry Story finds it to be quite insoluble in all solvents and that it is not attacked by acids or alkalis in the cold. Fuming nitric acid disintegrates it however.

The procedure of manufacture may be modified by adding the carbolic acid in small quantities from time to time to an excess of hot formaldehyde solution. Or the procedure may be reversed, i.e., the formaldehyde solution is added in small quantities to hot carbolic acid. A third modification is that of passing the vapor of formaldehyde through hot carbolic acid.

De Laire.

From the phenol alcohols hard translucent resins used as substitutes for copal, amber and shellac were produced through a process involving heating under diminished pressure by De Laire.³⁹ The phenol alcohols were prepared by condensing formaldehyde with phenol, cresol or menthol. The phenol alcohol was placed in a capacious receiver and melted. A vacuum was drawn and the heating continued at a temperature near the boiling point of the phenol alcohol so long as any water was given off. In the case of the alcohol from cresol the heating is continued until the mass solidifies. Solidification does not occur in the case of the ortho or para phenol-alcohol $C_6H_4(OH).CH_2OH$ but the end of the reaction is indicated by the appearance of copious white fumes and on cooling a hard transparent resinous mass is obtained. From saligenin a homogeneous pale yellow resin results which is insoluble in alcohol and melts at a temperature somewhat above $110^{\circ} C$. It is scratched by the finger nail with difficulty. The resin from saligenin resembles gum-lac. The resin from para oxybenzyl alcohol

³⁹ Fabriques de Produits de Chimie Organique De Laire, British Pat. 15,517, 1905; German Pat. 189,262, July 19, 1905.

is somewhat similar in properties. It melts above 115° C. and the specific gravity is 1.06. These products are soluble in hot caustic soda and are precipitated from solution by acids. Oil of camphor and terpineol act as solvents.

Infusible Resin.

The alcohol derived from para cresol when heated in this manner forms a transparent resin which is quite hard and heavier than water. When heated above 200° C. it softens but does not melt. At about 300° C. the resin begins to carbonize. The resins obtained from the cresyl alcohols are comparable in some respects with the copals.

Phenol alcohols can be condensed with certain other organic bodies to give resins of value in the plastic field. It has been pointed out by De Laire⁴⁰ that condensation of phenol alcohols with aniline, nitro-cresol, phthalic anhydride and dioxydiphenylmethane yield resinous masses of utility. Condensation can be accomplished by the action of alkaline agents or by organic or mineral acids. It can be made under the influence of heat alone either in vacuo or exposed to the air or in a current of an inert gas. Condensation also can be carried out under pressure. When condensation is carried out under pressure by heat alone the phenol alcohol and the other substance which is to be condensed therewith are mixed and heated in an oil bath until water vapor begins to be evolved. The source of external heat is then removed as the temperature of the mass will rise due to the heat of the reaction. Two successive condensations have been observed, 1. A condensation taking place while raising the temperature to about 100° yielding resins which are soluble in alcohol and other usual organic solvents. 2. A condensation taking place at a temperature above 100° , the exact point varying in accordance with the substance which is being condensed with the phenol alcohol. There is a further evolution of water vapor and a hard transparent mass more or less colored is obtained. Polymerization occurs and on the degree of this change will depend the solubility. The product becomes less soluble in alcohol as polymerization becomes more advanced. The end product of all these condensation reactions is insoluble in alcohol.

A reaction mixture consisting of the following, 10 parts phenol alcohol, 1 part dioxydiphenylmethane, 15 parts water and 3 parts hydrochloric acid is agitated for several hours. The reaction mass is washed with water until neutral, then the product is heated in vacuo or in open air until the evolution of water ceases. The product on cooling forms a transparent mass soluble in alcohol and fusing at about 100° C. Approximately the same result is obtained by dissolving in alcohol 10 parts of phenol alcohol and 1 part of dioxyphenylmethane, heating in vacuo at a temperature of about 100° C. until the evolution of water vapor ceases.

Starting with formaldehyde one procedure is as follows: 10 parts phenol, 5 to 10 parts aqueous formaldehyde (40 per cent), and 10 parts of hydrochloric acid (15 per cent) are stirred for some time and excess of hydrochloric acid and phenol removed by washing. A plastic mass remains which is heated in

⁴⁰ Belgium Pat. to De Laire, 192,590, June 15, 1906.

the open air or under the pressure of an inert gas until, on cooling, solidification takes place rapidly. In general this is obtained after heating for one-half hour at about 140° C. A hard resin is derived resembling amber, the color varying from yellow to brilliant brown and the transparency being likened to that of glass. The resin is soluble in methyl and ethyl alcohol and also in caustic alkali.

A resin having approximately the same physical properties is obtained by carrying out the condensation in the foregoing manner, with the exception that an alkaline catalyst is used in place of hydrochloric acid. Phenol may be replaced by a homologue. Thus, for example, cresol may be condensed with formaldehyde in the presence of caustic potash.

2 parts of nitroresol and 10 parts of phenol alcohol dissolved in alcohol and then the latter removed by distillation will yield a resin on heating to 100° C. and maintaining the temperature at that point until water vapor no longer is expelled. Hydrochloric acid also may be added to serve as a catalyst. The resin obtained fuses below 100° C. and exhibits a greater resistance to shock than the preceding.

Phenol Alcohol and Aniline.

A mixture of 50 parts of phenol alcohol and 10 parts of aniline is heated in an oil bath at about 100°. The action is continued until the evolution of water vapor is at an end and test samples upon cooling show the resin has acquired the desired consistency. The melted mass then is molded. The resin obtained is transparent, is scratched with difficulty by the fingernail and possesses a slight solubility in alcohol and alkalis. A resin which is more soluble is derived by using a salt of aniline, for example the salicylate. This is condensed with phenol alcohol by heating.

Phenol Alcohol and Phthalic Anhydride.

4 parts of phenol alcohol and 1 part of phthalic anhydride are dissolved in alcohol, the latter removed by distillation and the residue heated on an oil bath at 100° C. Heating is checked when evolution of water appears at an end and a test sample solidifies to a transparent resin soluble in alcohol. By prolonging the action of heat a product is derived which is insoluble in alcohol. The following classes of substances are listed by De Laire having the power of modifying the properties of phenol alcohols presumably as a result of condensation, namely, aldehydes, ketones, polybasic acids and anhydrides, phenols, amines and hydrocarbons.

A thorough study of the synthesis of phenol alcohols was made by Auwers⁴¹ in 1907. He confirmed the results reported by previous workers that only ortho and para derivatives are obtained by the condensation of phenols and formaldehyde. His observations showed that especially with the homologues of phenol the para compound could be selectively formed by using the strongest alkalis such as caustic soda. Thus from para xylenol, caustic soda and formaldehyde at room temperature the para compound was obtained in practically quantitative yield. Some phenols form by-products which are derivatives of dioxydiphenylmethane. Meta xylenol, formaldehyde and slaked lime heated carefully to 50° C. afford a fairly good yield of ortho oxymesityl alcohol. Frequently, however, oily and resinous bodies arise which appear to be dioxydiphenylmethane derivatives.

Stephan's Condensation Product.

A "formic-aldehyde compound" was described by Stephan⁴² in 1906 which, in a way, may be regarded a precursor of present methods of making phenol-formaldehyde resins. Stephan used an alkaline con-

⁴¹ Ber. 1907, 40, 2524.

⁴² U. S. Pat. 812,608, Feb. 13, 1906.

densing agent (caustic potash) and employed formaldehyde in excess of equimolecular proportions. By heating to 100° C. condensation and polymerization occurred and a product insoluble in water but soluble in alkali was obtained which was stated to be of value as a disinfectant. Stephan's procedure was to heat in an autoclave 2 parts by weight of phenol, 1 part of caustic potash solution (40° B.) and 4 parts of aqueous formaldehyde. A violent reaction took place with rise in pressure of a half atmosphere. When this reaction subsided the composition was heated on a steam bath until on addition of acid a voluminous white powder separated.⁴³

Wetter⁴⁴ calls attention to the disadvantage of using mineral acids as catalysts owing to the difficulty of removal of the acid from the resin. The presence in the resin of acid bodies is deleterious for some purposes. Acid salts such as ferric chloride may however be used advantageously. With small quantities of this catalyst a soluble resin is obtained but with larger quantities the formation of the resin is accompanied by a violent reaction and the resin is insoluble in most solvents. Other catalysts proposed by Wetter are ammonium chloride, sulphate and nitrate, potassium carbonate, potassium bisulphate, sodium sulphite. Procedures given by Wetter are as follows: 1000 parts phenol and 800 parts 40 per cent formaldehyde, in which about 25 parts ferric chloride have been dissolved, are warmed on the water bath until separation of an oil takes place. This oil is dissolved in ether, washed, dried and heated to obtain a resinous body of yellowish or brown color easily soluble in alcohol. Or 100 parts each of phenol and formaldehyde solution and 5 parts potassium bisulphate are heated to boiling. The oil which separates is extracted with toluene, the solution washed and after evaporation of the toluene 25 parts of formaldehyde are added, the heating being continued in an open vessel. The temperature may be raised finally to 160° C. yielding directly a clear yellowish-brown resin. In a similar manner 100 parts each of phenol and formaldehyde with 30 parts neutral sodium sulphite are heated in an open vessel until thickening is observed. The temperature is raised slowly to about 130° C. the mixture solidifying to a hard vitreous mass. This product is insoluble and infusible and can be turned in a lathe, ground and polished or colored with dyes.

⁴³ In 1905 Henschke (German Pats. 157,553 and 157,554; J. Chem. Soc. 1905, 88, i 429) found that an alkaline solution of phenol, heated with formaldehyde at 100° C. in an autoclave, lost its phenolic odor. Acids precipitate a bulky, pale yellow powder, insoluble in water or chloroform, soluble in alcohol, acetone, dilute sodium hydroxide, or ammonia. It decomposes on heating or on boiling its alkaline solution. A powder intended for medicinal use was made by Sternberg, U. S. Pat. 761,260, May 31, 1904, by reacting on wood tar with formaldehyde and hydrochloric acid. A condensation product of phenol or thymol with formaldehyde was prepared by Hilderbrandt, U. S. Pat. 876,311, Jan. 7, 1908, hydrochloric acid likewise was used as a condensing agent. Dürkopf, U. S. Pat. 598,914, Feb. 15, 1898, and Hock, U. S. Pat. 607,172, July 12, 1898, obtained condensation products of tannin and formaldehyde or hexamethylenetetramine.

⁴⁴ British Pat. 28,009, 1907, Knoll & Co.

Cresol Resin.

500 parts of commercial cresol from which orthocresol has been removed, 370 parts formaldehyde and 10 parts of ammonium chloride are heated to boiling until a colorless oil separates. When separation is at an end a vigorous current of steam is blown through the mass to remove excess of cresol and any uncombined aldehyde. After thus heating for about an hour a further addition of 10 parts of ammonium chloride is made and the heating continued until a white brittle resinous mass is obtained on cooling a sample. The product is washed thoroughly with hot water. In another case 500 parts cresol, 400 parts formaldehyde and 20 parts of sal ammoniac are heated at the temperature of the water bath until separation of an oil has become complete, then toluene vapor is blown through the batch. In this way formaldehyde and cresol are removed. When the batch becomes cloudy the introduction of toluene vapor is stopped. On removal of traces of toluene, for example, *in vacuo*, a clear transparent resin soluble in alcohol results. Various fillers may be added to the resinous composition and the aqueous formaldehyde may be replaced by hexamethylene-tetramine.⁴⁵

Lebach⁴⁶ secures rapid hardening of phenol-formaldehyde resinous compositions by using as condensing agents inorganic or organic acid chlorides, sulphuric acid esters, aluminum chloride and various salts. One procedure involves the heating of 1000 parts each phenol and aqueous 40 per cent formaldehyde with 100 parts of crystallized sodium sulphite. A light yellow viscous liquid is formed which is cooled and treated with 600 parts of wheat starch and 200 parts of 20 per cent sulphuric acid. The mass is heated in a mold at 85° C. for 1 to 2 hours. The product is a hard lustrous insoluble article. In another case phenol, formaldehyde and sodium sulphite in proportions as given above are heated for a short time, then 500 to 600 parts are distilled off and the residual liquid is well mixed with 600 parts of wheat starch. 150 parts of a mixture made in the proportion of 1 part sulphuric acid to 9 parts of glycerol are added in the cold and the product is heated in molds to 60° C. for half an hour. This gives a solid article of brilliant surface, free from pores. The articles may be washed with soda solution or exposed to ammonia fumes to neutralize the acid. Subsequent heating to about 100° C. improves the hardness and strength. In place of the mixture of sulphuric acid and glycerol 10 parts of a 25 per cent aqueous solution of sodium bisulphite or 5 parts of benzoyl chloride may be used.

⁴⁵ Moschatos and Tollens found the reaction product of hexamethylene amine on phenol, $C_{11}H_{12}N_4 \cdot 3C_6H_5O$, to decompose at 115-124° C. Pyro-catechin gave the compound, $C_8H_{12}N_4 \cdot 2C_6H_4(OH)_2$, a crystalline substance which became brown at 140° C. and a tar at 156° C. Resorcin yielded $C_8H_{12}N_4 \cdot C_6H_4(OH)_2$, decomposing at 190-200° C. *Ann.* 272, 271; *Ber.* 24, 695; *Ber.* 27, 238.

⁴⁶ U. S. Pat. 965,823, July 26, 1910, Knoll & Co. The Wetter patent immediately preceding, from its derivation through Knoll & Co. probably represents a development by Lebach.

Grognot⁴¹ attempts to minimize the violence of the reaction between phenol and formaldehyde in the presence of hydrochloric acid by using glycerol as an ameliorating agent. He first reacts on glycerol with formaldehyde in the presence of hydrochloric acid and subsequently treats the reaction products with phenol. A recommended procedure is the following: 2 parts by weight each of glycerol and formaldehyde are mixed and 0.3 to 0.4 parts of hydrochloric acid (21-22° B.) are added. The mixture is heated until a slight ebullition occurs and reaction progresses spontaneously thereafter without external heating. However when the reaction has subsided, heat may be applied for 1 or 2 hours, avoiding vigorous boiling. The mixture is cooled to 80° C. and 2 parts by weight of phenol crystals are added. Reaction takes place without further heating and is accompanied by a slight ebullition. A thick oil forms above the aqueous liquid containing glycerol. The oil is washed and dried, then heated to about 150° C. at which temperature it is maintained until a test sample shows a hard and brilliant resin has been formed.

⁴¹ U. S. Pat. 906,219, Dec. 8, 1908; French Pat. 390,713, 1907; 392,978, 1907; British Pat. 16,528, 1908; J. S. C. I., 1909, 99, 152; Chem. Abs. 1910, 4, 2745.

Chapter 7.

Phenol-Formaldehyde Resins. Bakelite, Condensite, Redmanol and Miscellaneous Phenol-Formaldehyde Resins.¹

From the preceding chapter we note, during the first decade of the present century, an increased activity in the study of phenol-aldehyde resins and their applications as substitutes for shellac and other resins in varnishes and in plastic compositions as binders.

During the latter part of that decade, Baekeland began an investigation of the resinous condensation products of phenol and formaldehyde, which brought forth yet another modification of these resins. He improved the methods of hardening under heat and pressure so that rigid-molded articles could be very readily obtained. The result of his investigations was the commercial development of the molding composition and product known as Bakelite. A great variety of applications have been made of phenol-formaldehyde resins or resinoids ranging from the manufacture of a billiard ball to wireless telegraphic apparatus; from the manufacture of a self-starter for automobiles to transparent fountain pens and artificial amber. The range of applications also embraces such articles as switchboards for battleships, molded parts for kodaks, phonograph records, casings for instruments of precision, armatures and commutators for dynamos and motors, telephone receivers, railroad signalling devices, grinding wheels, umbrella handles, buttons, cigar holders and pipe stems and ornamental articles.

To a notable extent the uses to which phenol-formaldehyde resins have been put in the plastic field have been spectacular ones and these products of late years during the period of commercial development and expansion have therefore been particularly before the public eye. Such varied applications as radio apparatus, billiard balls, pipe stems, beads, fountain pens and other articles constantly in evidence have led many to believe the importance of these resins in the plastic field is greater than the actual consumption of such products would warrant.

¹ There is no concise term for *resinous phenol formaldehyde condensation products*. This accurate but cumbersome expression has been abbreviated to "phenol condensation products," a loose term very properly open to criticism because of indefiniteness. The number of *non-resinous* phenol condensation products is legion and probably most of them are not convertible into resins, at least in any direct manner. The shortest descriptive expression appears to be *phenol-formaldehyde resins*.

Aside from the two most important organic plastics,—namely rubber and celluloid,—other plastic compositions, particularly those made from shellac and the pitch or asphaltic compositions made by the cold molding process described in Chapter 26, are employed in greater quantities than those having as a basis phenol-formaldehyde resins.² Owing to the enormous demand for shellac in the production of phonograph records this binder ranks at the head of the list in point of consumption of resinous plastics. Next in importance from this standpoint is the cold molded material.^{2a} In both of these fields the consumption is greater than in the case of the phenol-formaldehyde resins. In the United States the production of molding compositions containing phenol-formaldehyde resins, under the names of Bakelite, Condensite and Redmanol, has been restricted practically to three concerns, the rights of manufacture having been closely retained by the owners of the principal patents.³ In consequence, the molder requiring such compositions purchases the material from the sources mentioned paying therefor a price which roughly represents one-half the cost of the molded article, that is, the cost of the composition and labor is about equal. In view of the degree of publicity which phenol-formaldehyde resins have been accorded and their uses in a number of striking ways there has been possibly an unwarranted degree of activity among inventors in adding to, modifying and transforming phenol-formaldehyde resins. The result has been a host of patents on the subject which offers no small amount of labor to one desirous of becoming familiar with the art from the patent standpoint. The author has attempted to digest all patents on the subject which have come to his notice, and it is believed that in the following pages a very complete survey will be

² The 1921 production of synthetic phenolic resins by three firms was 1,643,796 pounds, compared with a production of 4,659,680 pounds during the previous year. Sales in 1921 amounted to 1,674,456 pounds, valued at \$1,352,166. (Report of Tariff Commission, Oil, Paint & Drug Reporter, 1922, 101, 19.)

^{2a} In the plastic field, products made by the process of cold molding employing pitch, asphaltum and similar binders, according to methods introduced into this country by Hemming in 1909, represent an industry of considerably greater magnitude than that thus far developed with hot molded plastics of the phenol formaldehyde resin type. Cold molding has reached its prominence owing to the relatively low cost of the raw materials, the far greater rapidity of molding and the higher heat resistance generally exhibited by these compositions. In fact the cold molding method has become one of the most important means of manufacturing heat resistant plastics prepared with organic binders. For further details see Hemming, *Plastics and Molded Electrical Insulation*, New York, 1923.

³ During the early stages of Bakeland's commercial development Aylsworth and Redman independently began the manufacture of the related products Condensite and Redmanol respectively and in 1916 a controversy took place between Bakeland, Redman (and associates, Weith and Brock) and Brown partly over the bearing of Redman's process on Bakeland's inventions. See *J. Ind. Eng. Chem.* 1916, 473; 568; 1077; 1172. (Note also Bakeland, *ibid.* 1910, 478; 1911, 518; 1914, 167; 1914, 263.) Patent litigation finally led to a consolidation of these competitive interests and the products, Bakelite, Condensite and Redmanol, which are well known to the molding trade in this country, now are controlled by the Bakelite Corporation.

found of the activities of inventors in this field during the past ten years. However space precludes any extended mention and the purpose of that material which is reviewed is rather to indicate to the reader the keynote of any particular investigation, thereby giving those wishing to pursue the subject further the opportunity to investigate the original literature.^{3a} If a good portion of the zeal which has been put into the study of modifications of phenol-formaldehyde resins or of making additions thereto for the purpose of accomplishing only a minor change in physical characteristics could have been applied to the problem, for example, of accelerating the molding operation or producing a pure white molding compound or increasing the strength and appearance of cold molded products, without greatly increasing their cost, it is safe to assert that a greater measure of progress would have been made in the field of resinous plastics.

The condensation products of phenols and aldehydes represent a wide range of substances and comparatively few of this enormous list of compounds are resinous. Of these a still smaller number are eligible as practical substitutes for natural resins or for use in molding compositions. For example phenol itself and meta and para cresol furnish useful resins with formaldehyde but ortho cresol is not serviceable in the production of thermo-setting molding compositions and usually is separated with great care from crude cresol. Ortho cresol products will not properly harden in hot pressing like the others mentioned, and as one progresses into the field of higher homologues of phenol the proportion of inert or non-resin-forming or crystalline bodies increases.

So many terms have crept into the descriptive matter relating to the resinous condensation products of phenols and formaldehyde that much confusion exists. In the present volume the various fanciful names urged by different investigators have not been used regularly in the text; the longer terms of *soluble fusible resin* and *insoluble infusible resin* being considered desirable for the sake of clarity. There may be indeed a degree of inappropriateness in using the term resin to apply to substances which in many cases do not possess all those properties common to the natural resins. In some of Baekeland's writings he refers to certain of the products in an advanced stage of condensation as "resinoid" substances. This perhaps is better usage than the term *resin* for such products.

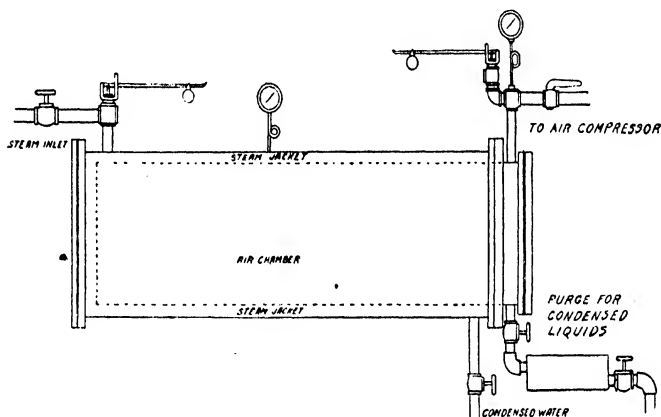
In beginning the study of the resinoids of phenol and formaldehyde, one may, to advantage, bear in mind that *saligenin* or phenol alcohol is a typical primary or parent substance. From it by water elimination and condensation arise the soluble fusible resins, the *saliretins*. A better term, at least one more easily remembered, would be "saliresins."

^{3a} Owing to the large number of patents which have appeared on the subject of phenol-formaldehyde resin, confirmation of these through tests conducted by the author obviously is impossible and the author therefore cannot personally endorse the correctness of statements appearing in patents and publications from which quotations or abstracts have been made. This comment applies to the other chapters of the book as well as the present one.

Under the term "Novolak" Baekeland embraces these soluble fusible resinous products. From the soluble fusible products, the saliretins, the insoluble infusible resinoids are obtained by further or more deep-seated condensation.

Stages of Reaction.

A study of the nature of condensation between phenol and formaldehyde led Baekeland to conclude that the reaction, instead of occurring in two stages, was capable of being carried out in three distinct phases.*



Courtesy of General Bakelite Company.

FIG. 3.—Bakelizer. This apparatus is simply a container in which phenol-formaldehyde resins can be heated under pressure. Carbon dioxide or other gas is supplied to the bakelizer to create a pressure of several atmospheres on the resin which is undergoing hardening. Sufficient pressure is applied to counteract the tendency of the resin to become spongy due to the escape of gas when heat is applied. This apparatus has been used experimentally but finds very few commercial applications.

By separating the reaction into these phases Baekeland was able to prepare an intermediate condensation product. The three phases of reaction can be described as follows:

First Phase. The formation of an initial condensation product which Baekeland designates as A.

Second Phase. The formation of an intermediate condensation product designated as B.

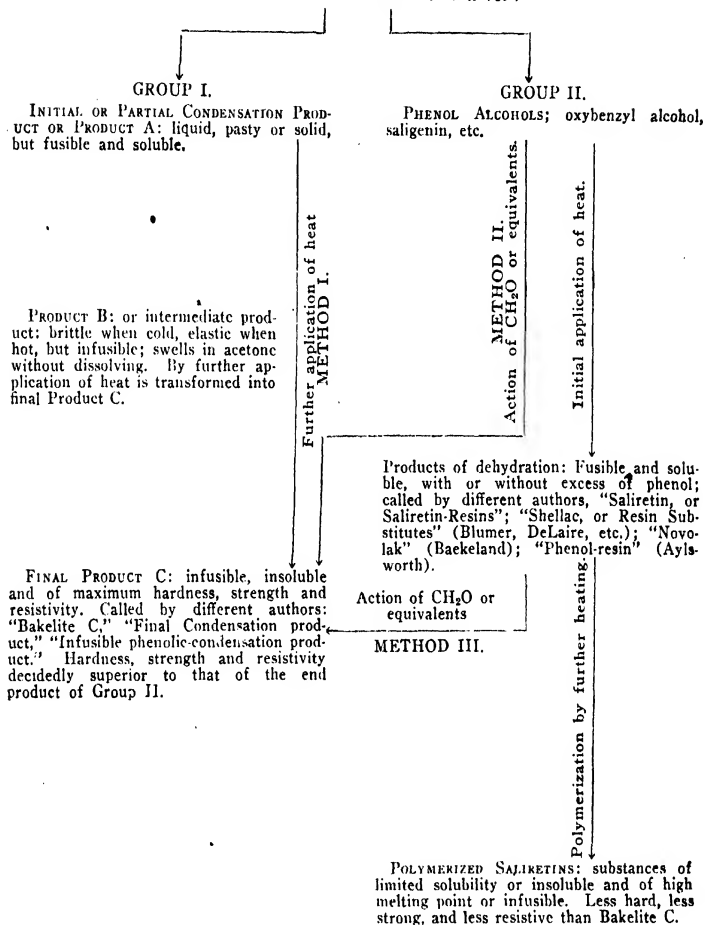
Third Phase. The formation of a final condensation product C.

A, at ordinary temperatures, may be liquid, or viscous, or pasty, or solid. Is soluble in alcohol, acetone, phenol, glycerol and similar solvents; is soluble in NaOH. Solid A is very brittle and melts if heated. All varieties of A heated long enough under suitable conditions will change first into B and then finally into C.

*J. Ind. Eng. Chem. 1909, 155.

BAEKELAND'S CLASSIFICATION.

Phenol and Formaldehyde (or equivalents) under varying reacting conditions form different bodies. (J. Ind. Eng. Chem. 1912, 4, 739.)



B is solid at all temperatures. Brittle but slightly harder than solid A at ordinary temperatures: insoluble in all solvents but may swell in acetone, phenol or terpineol without entering into complete solution. If heated, does not melt but softens decidedly and becomes elastic and somewhat rubber-like, but on cooling becomes again hard and brittle. Further heating under suitable conditions changes it into C. Although B is infusible it can be molded under pressure in a hot mold to a homogeneous, coherent mass, and the latter can be further changed into C by the proper application of heat.

C is infusible, insoluble in all solvents; unattacked by acetone, indifferent to ordinary acids, of greatly improved resistance to alkaline

solutions; is destroyed by boiling concentrated sulphuric acid, but stands boiling with diluted sulphuric acid; does not soften to any serious extent if heated, stands temperatures of 300° C.; at much higher temperatures begins to be destroyed and chars without entering into fusion. It is a bad conductor of heat and electricity.

The preparation of these condensation products A and B and their ultimate transformation into C for technical purposes Baekeland states constitute the so-called Bakelite process.

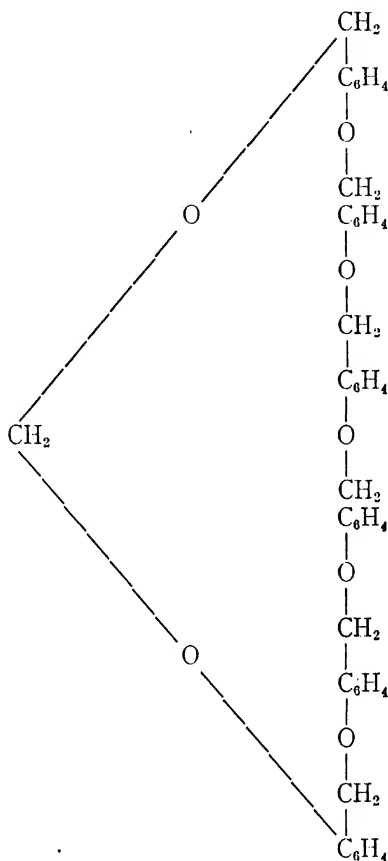
Constitution of Phenol-Formaldehyde Resins.

Starting with oxybenzyl alcohol and formaldehyde Baekeland^{*} determined that unless at least 1 mol. of formaldehyde to 6 mols. of oxybenzyl alcohol was used Bakelite was not obtained but instead a product containing saliretin compounds. The same result was stated to occur by heating 6 mols. of phenol and 7 mols. of formaldehyde in the presence of a small amount of a base. If less formaldehyde is used or if, for some reason, all the formaldehyde does not enter into reaction, the resulting resin is still attacked by acetone. In the course of his early researches on the constitution of Bakelite, the proposal was made by Baekeland that his product in its simplest form was a polymerized oxybenzyl methylene glycol anhydride. If made from ordinary phenol the reaction could be represented by $n(6C_7H_8O_2 + CH_2(OH)_2) = n(C_{43}H_{38}O_7) + n(7H_2O)$. The stages of formation of Bakelite were explained on the ground that Stage A consisted in the formation of a partial anhydride of a phenol alcohol and methylene glycol containing hydroxyl groups and therefore reactive with sodium hydroxide. Stage B was supposed to be due to the formation of a higher anhydride by the further elimination of water. This higher anhydride was supposed to no longer possess hydroxyl groups but to be capable by addition of sodium hydroxide to form alkaline compounds. Stage C was explained on the ground that it resulted from the polymerization of the B product.

Baekeland recounts the following experiments in support of the views expressed above: if a mixture of phenol and formaldehyde with a small amount of base is heated in a sealed glass tube, the product A results with the separation of the mixture into two layers; the product A being present in the lower stratum. This occurs also if anhydrous phenol is heated with paraform in the presence of a small amount of base. When A, free from moisture, is introduced into another sealed tube and heated carefully the intermediate condensation product B results with the liberation of additional water. The mass B has not contracted in volume to an important extent. After freeing B from water if it be heated in a sealed tube transformation occurs into the product C but in this case there is no further elimination of water. On the other hand there is a decided contraction in volume. This contraction together with the remarkable increase in physical and chemical inertness Baekeland believes signifies that C is simply a polymer of B.

^{*}J. Ind. Eng. Chem. 1909, 159.

A structural formula originally proposed by Baekeland is the following:



The above formula has been criticized by other investigators and various proposals have been made setting forth other structural formulae. However, the inability to isolate the resinoids of Bakelite in a state of purity makes any endeavor to delineate its constitution a difficult matter. Baekeland very fittingly expresses the situation as follows:

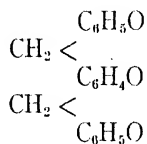
"One hypothesis is about as easy to propose as another as long as we are unable to use any of the methods for determining molecular size and molecular constitution."^{5a}

By the direct action of phenol, 3 mols., with formaldehyde, 2 mols., Aylsworth^{5b} obtained a fusible, soluble resin without resorting to con-

^{5a} J. Ind. Eng. Chem. 1913, 506.

^{5b} U. S. Pat. 1,020,593, Mar. 19, 1912.

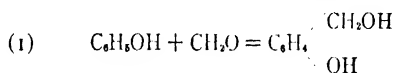
densing agents or catalysts. He termed this substance "phenol resin" and assumed its constitution to be



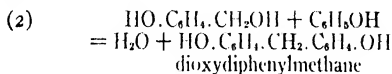
In discussing this structure, Lebach⁵⁰ calls attention to the fact that there is no justification for the formula other than that based on the relative proportions of the ingredients employed. Lebach also notes that the resin obtained according to the procedure furnished by Aylsworth will contain decided amounts of free phenol. Baekeland⁵¹ observes that all the phenol-formaldehyde resins of the fusible type may be composed of two or several individual chemical bodies mixed in varying proportions and forming a colloidal solid solution. This, he states, applies to any of these resins, whether they are obtained by direct action of phenol on formaldehyde or whether they are made step by step by the intermediary formation of phenol alcohol and subsequent dehydration thereof. Some of these substances may or may not be simple dehydration products of phenol alcohols derived therefrom by simple union of several molecules with elimination of water, after the same reaction by which ether or ethyl oxide is formed by the elimination of water between two molecules of alcohol. Or, again, the process of dehydration may possibly be complicated by more far-reaching transformations, transpositions, or rearrangements of the molecule.

Raschig⁶ looks upon the reactions giving rise to the formation of Bakelite according to the following equations.

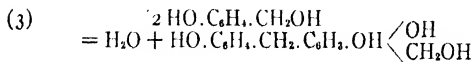
The first stage is that of formation of ortho- and para-oxybenzyl alcohols



The alcohol thus formed may react in two ways. It may combine either with phenol or with a second molecule of the oxybenzyl alcohol. With phenol the reaction is



When two molecules of oxybenzyl alcohol unite the reaction is as follows:



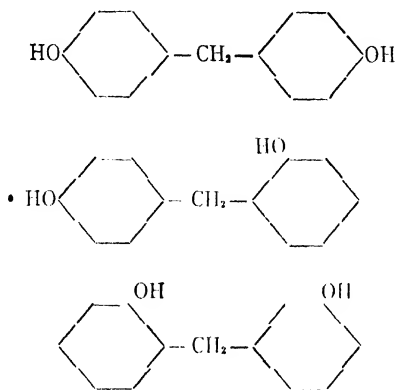
Raschig thinks it more probable that the reaction takes place according to (3). The di-alcohol formed can react further with phenol or with mono- or

⁵⁰ J. S. C. I. 1913, 559.

⁵¹ J. Ind. Eng. Chem. 1913, 506.

⁶ Z. anorg. Chem. 1912, 25, 1945.

di-alcohols. Assuming, however, the reaction to be that between oxybenzyl alcohol and phenol giving rise to the formation of dioxydiphenylmethane three isomeric forms are possible.



As yet no investigations have been made which throw much light on the further course of the reactions. When studying resinous products of this character there is great difficulty in isolating the component parts in a state of purity and to determine the constitution of a resinous substance as complex as Bakelite presumably would require a vast amount of research.

Raschig endeavors to explain the difference between the soluble and insoluble resins derived by the condensation of phenol and formaldehyde in this way. Soluble resins arise when treating 1 Mol. of phenol with less than 1 Mol. of formaldehyde, as a rule only .5 Mol.; while infusible resins are formed when 1 Mol. and as a rule 10 to 20 per cent more than this are employed for 1 Mol. of phenol. Also the soluble resins can be converted into insoluble resins of the Bakelite type by warming with additional formaldehyde. If 1 Mol. of phenol to 0.5 Mol. of formaldehyde are employed the normal smooth course of the reaction would involve conversion only to dioxydiphenylmethane as further change is checked through lack of formaldehyde. However as a smooth reaction is not indicated its course is more probably in the direction of producing a mixture of 3 isomeric diphenylmethanes, some alcohols of these bodies while some unchanged phenol remains in the composition. The relatively low molecular weights of the compounds arising in this case determine its easy solubility.

Insoluble Resins.

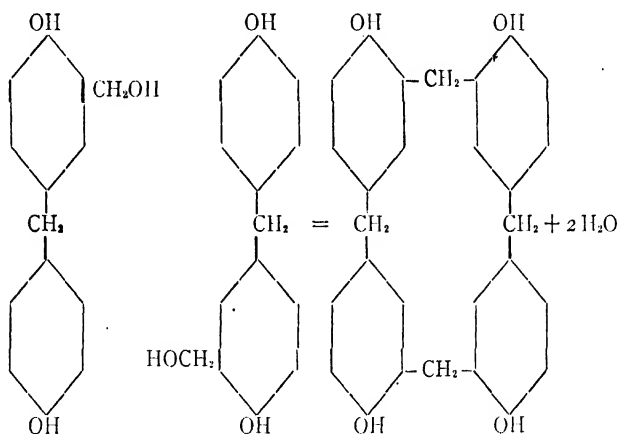
With larger amounts of formaldehyde not only the dioxydiphenylmethanes are formed as above but very substantial quantities of the alcohols. These may be expected to react again with phenol or with dioxydiphenylmethane and thus by such interaction a molecule of relatively great size is developed. Because of its high molecular weights its reactions are sluggish and its insolubility is low or nil. In such a manner, according to Raschig, a resinoid substance of the character of Bakelite is formed. Baekeland does not fully agree with Raschig's conclusions for he calls attention to an oversight by Raschig with regard to the influence of the nature of the condensing agent as a determining factor with respect to the formation of fusible or infusible products. He states that in the presence of small amounts of bases infusible condensation products will result whether or not an excess of phenol is present.¹ Baekeland comments further:

"I take the liberty of pointing out that this theoretical interpretation holds

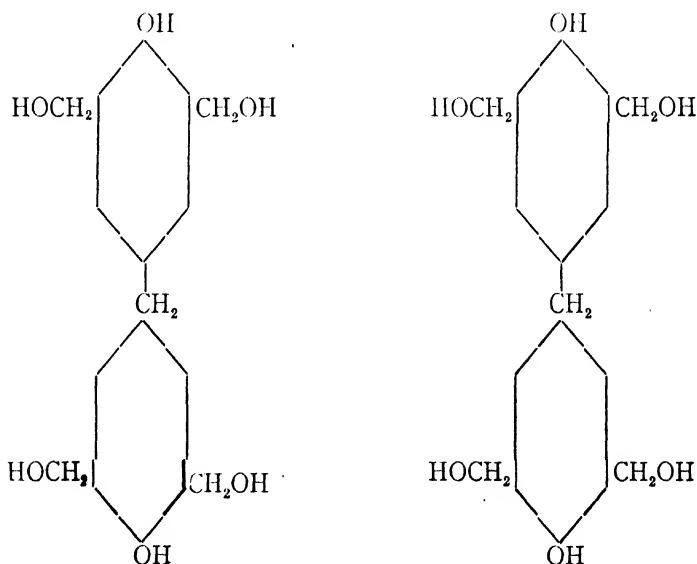
¹ J. Ind. Eng. Chem. 1913, 506.

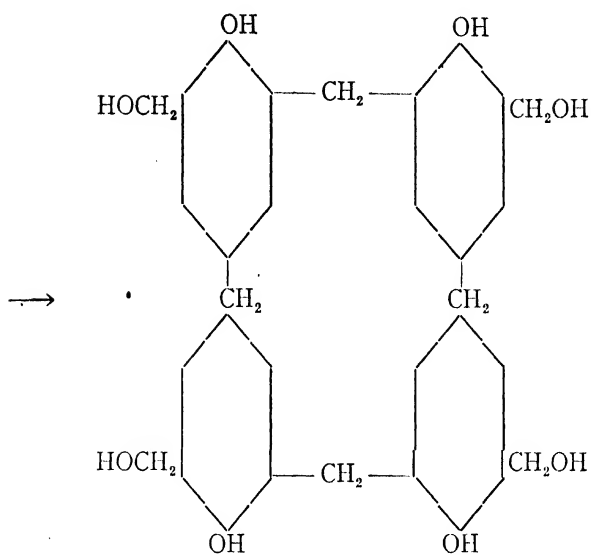
good only to a certain extent. If it is possible, and even probable, that some of the bodies mentioned by Dr. Raschig exist in the first phases of the reaction, or may exist in the final products together with an endless variety of other chemical individuals, we know next to nothing of the relative importance thereof, whether they exist as traces, or whether they play a fundamental rôle."

In the construction of the highly complex molecule Raschig indicates additional possible reactions. These are based on the assumption that diphenylmethane derivatives are the main products in this process. 1 Mol. of ortho-alcohol and 1 of the para-alcohol may combine to a body represented by the following:

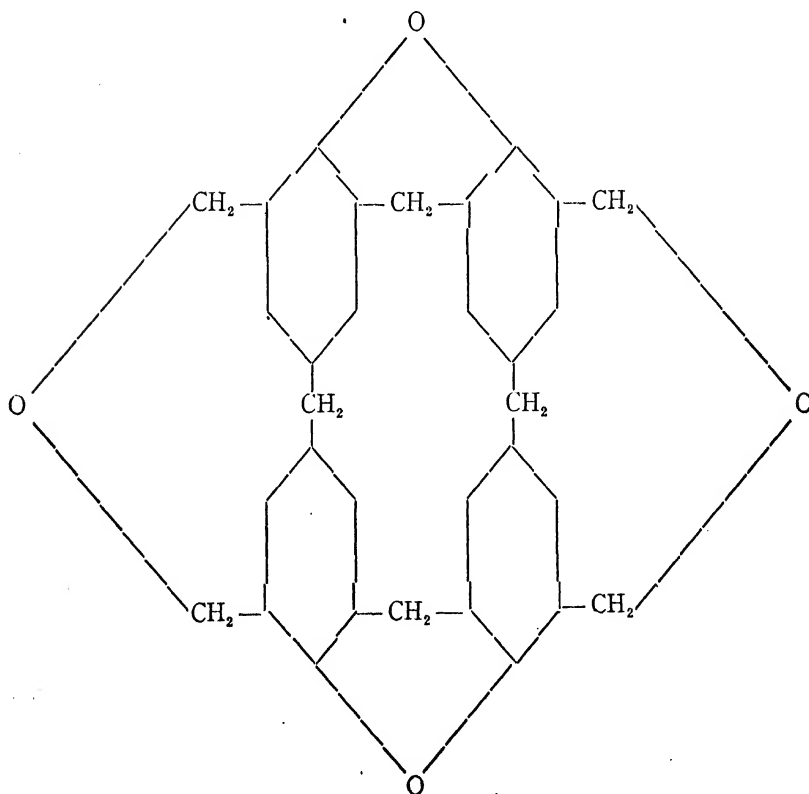


From reaction mixtures containing a larger proportion of formaldehyde even more complicated bodies may be obtained.





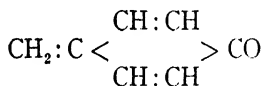
An even more complicated structure indicated by Raschig is the following:



In the course of some experiments made by Raschig⁸ ortho-oxybenzyl alcohol was treated alone with a condensing agent and did not yield an insoluble infusible resin. Paraoxybenzyl alcohol reacted in the same manner, while from a mixture of the two alcohols an insoluble resin was obtained. From this Raschig concluded that both the ortho and para compounds were necessary for the production of a product of the Bakelite type. Baekeland⁹ investigated this point and found that when the ortho or the paraoxybenzyl alcohol or a mixture of equal parts of both alcohols with a small amount of ammonia or caustic soda were heated in a sealed tube for several hours at 160° C. products were obtained which were similar to the resins of the polymerized saliretin type. They softened on heating but were infusible, were much more brittle than more highly reacted resinoids and were immediately acted on by acetone or caustic soda solution. Baekeland heated para oxybenzyl alcohol with 5 per cent of paraform in a sealed tube and obtained an infusible product of great hardness and not attacked by acetone or caustic soda solution. Baekeland therefore concluded that the products obtained by Raschig had not been converted to the maximum degree of hardness and chemical resistivity due to insufficient formaldehyde.

Tautomeric Phenol.

Wohl and Mylo¹⁰ have advanced a radically different hypothesis which considers these bodies to be polymerization products of the methylene derivatives of tautomeric phenol corresponding to the formula



Polymerization.

Experiments made by Jablonower¹¹ confirm the theory that first a stage of condensation occurs succeeded by one of polymerization. Jablonower carried out a series of tests on viscosity with various proportions of formaldehyde and catalyst. With more than 6 per cent of the condensing agent and at temperatures of 80° C. and above a decrease in the rate of viscosity change occurs. From these observations Jablonower concludes that beyond these limits the condensation is soon completed, after which the increase in density is due to polymerization. He heated some of the reaction mixtures at a temperature of 110-120° C. for 2-4 hours. During this time water was eliminated so rapidly that there was not sufficient time to evaporate. On cooling therefore a water layer separated. This was removed and the liquid again heated to the same temperature and an increase in density was observed but no additional water separated. The point where condensation ends and polymerization begins could not be definitely determined. Jablonower is of the opinion that polymerization sets in as soon as some condensation has taken place.

Van Voorhout's Investigations.

Van Voorhout¹² endeavored to determine the course of the reaction and the effect of different catalyzers by observations on the viscosity of the reaction mixture. His investigations showed that the strongest bases exerted the greatest condensing power and also that acids act differently than bases as condensing agents. With alkaline condensing agents van Voorhout was enabled to identify ortho and para oxybenzyl alcohol as intermediate products. In experiments on condensation in the presence of acids he heated calculated amounts of phenol and formaldehyde with 0.5 per cent sulphuric acid for 2

⁸ Z. anorg. Chem. 1912, 25, 1946.

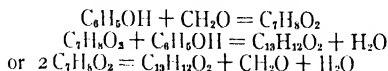
⁹ J. Ind. Eng. Chem. 1913, 506.

¹⁰ Ber. 1912, 45, 2046.

¹¹ J. Am. Chem. Soc. 1913, 35, 811.

¹² Dissertation, Delft; Chem. Weekblad 17, 2; Kunststoffe 1921, 11, 59.

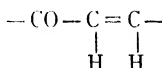
hours under a reflux condenser. From time to time water, lost by evaporation, was replaced. Two liquid layers were obtained, one an aqueous and the other a viscous product. From both of these layers dihydroxydiphenylmethane was separated. The reaction in part is expressed by the following



van Voorhout is of the opinion that Bakelite is principally dioxydiphenylmethane, presumably in polymerized form associated with traces of phenol and formaldehyde in solid colloidal solution.^{12a}

Theories of Herzog and Kreidl.

A different view is entertained by Herzog and Kreidl. These investigators do not consider the chain formula proposed by Baeckland to express the constitution of phenol formaldehyde resinous condensation products. Following Raschig's suggestions in part, Herzog and Kreidl look upon the structure of the alkali resistant product as either quinoid or of a desmotropic character. They favor the latter, since transformation during resinification to the quinoid form is less probable. Herzog and Kreidl suggest the presence of the unsaturated resinophore group:



supposedly the result of desmotropic change, to be the cause of the resinification. On pages 106 and 107 are given the two forms proposed by Herzog and Kreidl.¹³

Gsell's Observations.

Gsell¹⁴ has reached the conclusion that condensation products are formed in all reactions which yield hydroxy-benzyl alcohols or aldehydes. Thus from resorcinol and methylene chloride in the presence of alkali, dihydroxybenzyl alcohols are obtained, which on heating are condensed to solid products. Again by the interaction of phenol and chloroform in the presence of alkali, hydroxy-benzaldehyde is obtained as a primary product, and this, by the further action of alkali, is decomposed into a hydroxycarboxylic acid and hydroxybenzyl alcohol which condenses as a plastic mass when heated. Similar condensation products are obtained by the interaction of phenols and ketones in the presence of hydrochloric acid. For example solid substances are produced by boiling 50 cc. of acetone and 50 grams of resorcinol with 3 to 5 cc. of strong hydrochloric acid.

Amphoteric Properties.

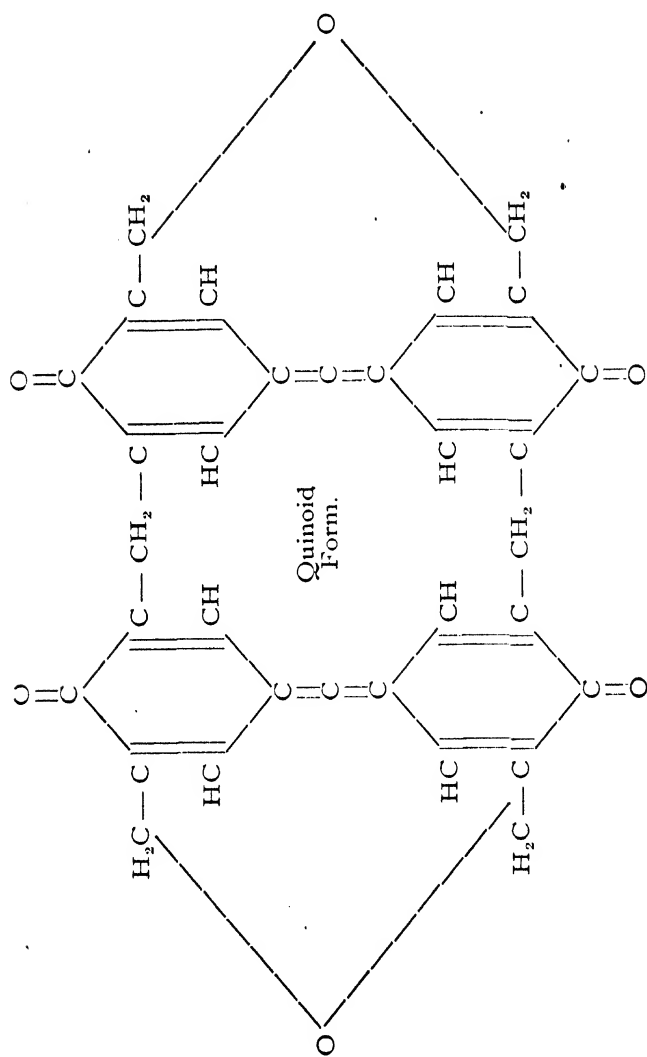
Phenol-formaldehyde resinous condensation products and protein show certain similarities in their physical and chemical properties. Sato and Sekine^{14a} attribute these to amphoteric conditions. When the

^{12a} Commenting on van Voorhout's investigations Drummond (J. S. C. I. 1922, 41, 522R) believes further practical advance can more readily be achieved by what he terms a synthetic study of the resin, that is by investigating it before and during synthesis rather than analytically after the synthesis has taken place. Such a study would involve a physical as well as a chemical examination. It should include the changes taking place during condensation in such physical properties as viscosity and density.

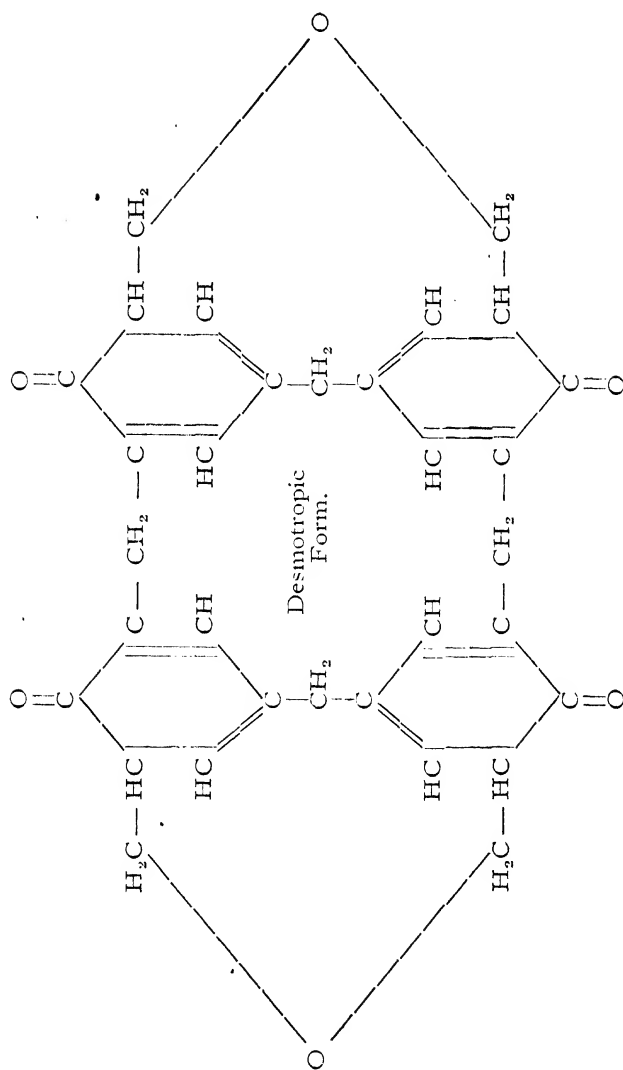
¹³ Z. angew. Chem. 1922, 35, 641.

¹⁴ Chem. Z., 1914, 38, 541.

^{14a} J. Chem. Ind. Japan, 1921, 494; Chem. Abs. 1922, 1133.



Quinoid Structure Proposed by Herzog and Kreidl.



Desmotropic Structure Proposed by Herzog and Kreidl.

condensation product is washed with water until neutral to litmus and is dissolved in acetone, it requires a great deal of alkali to cause phenolphthalein to turn red while with congo red more acid is required to obtain a blue coloration. When copper sulphate, which is weakly acidic, is added to such a neutral solution a characteristic dark yellow product is formed. Curiously, such a product will not become blue on the addition of ammonia. With lactic acid the yellow color disappears, indicating that the metallic salt compound is decomposed. On the other hand when a basic copper salt such as copper carbonate is added to the solution a brown colored product results which does not decolorize on the addition of lactic acid. Sato and Sekine consider this is indicative of union by copper sulphate at a different point from that resulting with copper carbonate. Ferric salts act similarly. The amphoteric property of the phenol formaldehyde condensation product is considered to be due to the acid hydroxyl group of phenol and the alcoholic group present in the molecule of hydroxy benzyl alcohol. According to this theory the product should combine with any hydroxy fatty acid or any other compound which contains groups $-\text{CH}_2\text{OH}$, $=\text{CHOH}$ or $\equiv\text{COH}$. Sato and Sekine report this to be the case and based on this principle they have prepared products analogous to Bakelite without the employment of high pressures.^{14b}

Influence of Different Catalyzers.

By the use of metallic salts such as copper carbonate, tin tetrachloride, ferric chloride and potassium ferricyanide Sato and Sekine^{14c} arrived at a classification of phenol-formaldehyde oily condensation products, according to which three groups exist; depending on the kind of catalyzers employed. (1). Soluble and fusible resins which are prepared by acid catalyzers give no color reaction with the above salts. In this group formaldehyde probably attacks phenol at the para position. (2). Insoluble and infusible resins which possess a moderate degree of strength and which are produced by the use of ammonia as a catalyzer. This group gives a dark greenish brown color with copper sulphate, a brown coloration with copper carbonate and a brownish red color with tin tetrachloride. Ferric chloride yields a yellowish brown coloration. Formaldehyde probably reacts at the ortho position. (3). The strongest resins representing the highest degree of condensation leading to an insoluble infusible product, according to these investigators, are obtained by the use of caustic soda or sodium bisulphite as catalysts. The color reactions are dark brown with copper sulphate, yellowish green with copper carbonate, light green with tin tetrachloride and reddish violet with ferric chloride. In this group formaldehyde perhaps unites at the meta position. The metallic salt combinations of these products can be broken up easily with lactic acid.

^{14b} Note Sato, Japanese Patent 37857, Jan. 18, 1921; Chem. Abs. 1922, 1301 and 39, 321, July 19, 1921; Chem. Abs. 1922, 2760.

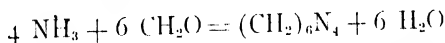
^{14c} J. Chem. Ind., Japan, 1921, 321; Chem. Abs., 1922, 1132.

Sato and Sekine^{14d} observe that the phenol formaldehyde oily condensation products prepared by using ammonia as a catalyzer can be fractionated into three components by means of differences in their solubility. A mixture in the proportions of 1 mol. of formaldehyde, 1 mol. of phenol and 0.1 mol. ammonia was heated at 90 C. for one hour and cooled. The resulting oily product was washed and when free from moisture yielded a transparent viscous material. When an excess of a saturated solution of copper sulphate was added to the product a dark brownish green substance was formed. The oil was then extracted with 95 per cent alcohol and the residue after drying was a yellow powder. The alcoholic extract when treated with ether gave a yellowish green precipitate. On dilution of the filtrate with water a white substance was obtained. These three components when treated separately with lactic acid easily part with copper and after such treatment when mixed a clear transparent viscous oil is again produced.

According to Sato^{14c} the fusibility of phenol-formaldehyde condensation products of the resinous type depends upon the combining capacity of formaldehyde with phenol, that is the number of alcoholic groups present in the oily viscous condensation products. If only a few alcoholic groups are present, fusible resins result, but if the number of alcoholic groups is large infusible and insoluble resins are obtained.

Hexamethylenetetramine, C₆H₁₂N₄.

This substance, also called *formin*, but more commonly by the abbreviation "*hexa*," always forms when ammonia and formaldehyde are mixed. Therefore when ammonia is added for catalytic purposes to a mixture of phenol and formaldehyde, hexa is produced, and the reaction forming a resin, as Baekeland has pointed out, progresses in the same favorable manner that is in evidence with basic catalysts generally. The reaction between ammonia and formaldehyde generates considerable heat and water is eliminated as follows:



The use of hexamethylenetetramine in preparing phenol-formaldehyde resins apparently was first noted by Lebach (see Wetter, p. 90). Obviously hexa, wet or dry, furnishes a convenient means of applying formaldehyde and a considerable number of processes are based on the expedient of employing hexa in lieu of formaldehyde and some other basic catalyst not reacting with this aldehyde in the manner characteristic of ammonia.

In the dry state, hexa is relatively expensive and therefore it represents a rather costly material for the preparation of initial or fusible resins. More frequently, as may be expected, it is employed in small proportion as a finishing or hardening agent. As Baekeland has indi-

^{14d} J. Chem. Ind. Japan, 1921, 332; Chem. Abs. 1922, 1133.

^{14c} J. Chem. Ind. Japan, 1921, 580; Chem. Abs. 1922, 1133.

cated^{14f} a fusible resin, transformable by heat to an infusible body, requires an added proportion of formaldehyde in its making, approximately 7 mols. formaldehyde to 6 mols. of phenol being required. This amount of course may be supplied all at once or in two or more stages. Making fusible resins with the aid of one catalyst and transforming to an infusible resin in the presence of another catalyst constitutes the basis of scores of processes differing but slightly in details. That hexa should be repeatedly advocated in such duplex processes is not surprising in view of its well known properties.^{14g}

Redman, Weith and Brock¹⁵ consider the reaction between hexamethylenetetramine and phenol taking place in aqueous solution to be substantially different from that progressing when the reagents are heated in a dry state. The simplest product which forms when phenol reacts with hexamethylenetetramine is the compound hexamethylene-tetraminetriphenol¹⁶ which is a crystalline product.

Wet Process Using Hexa.

When 1 mol. of hexamethylenetetramine and 6 mols. of phenol are boiled in aqueous solution a light yellow transparent viscous liquid separates and on continued heating increases in viscosity. At room temperature it becomes a brittle amber-like solid.

Dry Reaction Using Hexa.

Lebach¹⁷ states that hexamethylenetetraminetriphenol when heated in the dry state evolves ammonia and yields an insoluble and infusible substance. Lebach considered this product to be Bakelite but this is challenged by Redman who looks upon Bakelite as a material in which 6 phenols are united with 7 methylene groups. As hexamethylene-tetraminetriphenol has a composition of 6 phenols for every 12 methylene groups over 40 per cent more methylene is present than is required, according to Redman, to produce Bakelite. When hexamethylene-tetraminetriphenol is heated, besides ammonia there is evolved a substance having an odor somewhat resembling methylamine. The latter by-product is not present when the phenol is increased to 6 mols. of phenol for 7 methylenes. If, however, dry hexamethylenetetramine and anhydrous phenol are mixed, the mixture heated to 60° C. or higher a reaction begins with the evolution of ammonia which according to Redman's investigation is the only by-product. With the phenol in excess and if the mixture be heated to the boiling point the reaction proceeds with great rapidity. Nearly all the ammonia is evolved in

^{14f} J. Ind. Eng. Chem. 1909, 159.

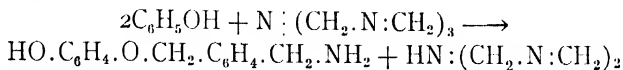
^{14g} See also this chapter, section on Catalysts. The structure of hexamethylenetetramine is still under discussion. Note the work of Dickinson and Raymond, J. Am. Chem. Soc. 1923, 45, 22. Also the interesting investigations conducted by Harvey and Baekeland, J. Ind. Eng. Chem. 1921, 13, 153.

¹⁵ J. Ind. Eng. Chem. 1914, 6, 3.

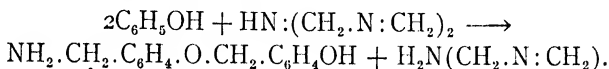
¹⁶ Moschatos and Tollens, Ann. 272, 280.

¹⁷ Z. anorg. Chem. 22, 1600.

the first 10 minutes boiling. The reaction according to Redman takes place in the following series of steps. Accepting the formula of hexamethylenetetramine as $N:(CH_2.N:CH_2)_3$ this reaction may take place as follows:



and a second reaction may occur



This process continues until all the CH_2 groups have combined with the phenol and ammonia remains as the by-product. The intermediate product aminosaligeno-saligenin has been isolated.

Hexa and an Excess of Phenol.

The heating of a mixture of hexamethylenetetramine with an excess of phenol produces resins of a soluble and fusible type (Novolak). These are soluble in alcohol, acetone, aqueous caustic alkali. On heating, the resin remains a liquid at temperatures up to $180^\circ C$. even after being subjected to this temperature for many hours. When cold the resin hardens to a glossy material which is more brittle than common rosin.

Excess of Hexa.

As the phenol is decreased below the ratio of 12 mols. to 1 mol. of hexamethylenetetramine the liquid thickens and the resin changes to an infusible and insoluble transparent substance of yellow or red color. 9 mols. of phenol to 1 mol. of hexamethylenetetramine yield a complex which is quite brittle in the cold and a rubbery mass when heated to $170^\circ C$. 8 mols. of phenol to 1 of hexa is brittle in the cold and when hot resembles polymerized tung oil. As the phenol is reduced the reaction product becomes less elastic when hot and in the ratio of about 5 mols. of phenol to 1 of hexa is quite hard at all temperatures. At room temperature it is a dense tough product, the tensile strength of which ranges from 4000 to 5200 pounds per square inch. Decreasing the phenol below 5 or 5.5 mols. to 1 of hexa renders the resin brittle due to the presence of an excess of crystalline hexa.

Evolution of Ammonia.

A mixture of phenol 6 mols. and hexa 1 mol. on heating strongly, for example, $180^\circ C$., evolves ammonia rapidly and produces a spongy material. This may be ground very readily and when pressed in hot molds under a pressure of 4-6 tons per square inch yields a homogeneous transparent solid article of good mechanical strength, high dielectric properties and quite inert to reagents. If the same mixture is heated on the water bath at $100^\circ C$. for 25 hours less than half of the total

ammonia will be evolved and the mass is viscous when hot, brittle when cold. Redman has succeeded in casting in open molds mixtures made in these proportions, allowing hardening to take place by heating without application of external pressure. Transparent rods 2 feet long and $1\frac{1}{2}$ inches in diameter free from fractures and gas bubbles were obtained.

Hexa and Cresols.

Researches conducted by Harvey and Baekeland^{17a} on the compounds of hexamethylenetetramine with cresols and analogous bodies show a wide variation in combining proportions and in the properties of the resulting compounds. While hexamethylenetetramine and ordinary phenol easily combine to yield the crystalline compound, *hexamethylenetetramine triphenol*, other phenolic bodies do not behave similarly. Of the cresols, the addition product of metacresol is most easily obtainable.

Harvey and Baekeland succeeded in preparing hexamethylenetetramine di-m-cresol. A mixture of 315 grams of m-cresol and 136 grams of hexamethylenetetramine was heated for an hour in 80 cc. of a 60 per cent (60 parts by volume of alcohol and 40 parts by volume of water) alcoholic solution. Too much heating caused the addition product to decompose and pass over into the non-crystallizing resinous material. By withdrawing portions of the mixture from time to time, and cooling slightly, it could be observed, by the formation of crystals, when the most favorable point was reached before resinification set in. On stopping the heating, crystals appeared even in the hot solution. The crystals were filtered off and pressed on a porous tile to get rid of the adhering sirupy material. The product was then dissolved in hot 95 per cent alcohol. On cooling, long, fine, needle-like crystals separated out. Analysis showed that the substance was not formed on a 1:3 basis as is the case with the ordinary hexamethylenetetramine triphenol, but was an addition product of 1 mol. of hexamethylenetetramine and 2 mols. of m-cresol. Hexamethylenetetramine di-m-cresol has not a true melting point, since when the substance is held at a temperature around its point of liquefaction, 90° C., it undergoes decomposition, passing over into the irreversible resinous stage.

Hexamethylenetetramine di-p-cresol.

The addition product has no melting point, but begins to resinify at the temperature of liquefaction, 87° C. The decomposition is shown when the substance turns brown and partially resinifies upon heating in a sealed glass tube for 3 hours at a temperature of 90-100° C.

Hexamethylenetetramine mono-o-cresol.

The compound behaves somewhat differently from the p- and m-cresol addition products, since on heating there was no sharp melting point to the liquid stage, followed by a final passing over to the resinous material. A small portion seemed to soften on heating and show signs of melting, but most of the substance either sublimed or charred.

That 2 mols. of para and metacresol unite with 1 mol. of hexamethylenetetramine while only 1 mol. of orthocresol combines with 1 mol. of the amine may find explanation in the structure assumed for the three cresols. The hydroxy group of the para and meta-cresols has on each side of it a hydrogen, while the hydroxy group of orthocresol has a hydrogen on but one side. From this it would seem that the extent of addition depends upon the number and activity of the hydrogens adjacent to the reacting hydroxy group.

^{17a} J. Ind. Eng. Chem. 1921, 13, 153; Hexamethylenetetramine-triphenol and phenol alcohols, see Baekeland, U. S. Pat. 1,442,420, Jan. 16, 1923.

Hexamethylenetetramine Hydroquinol.

On heating, part of the compound sublimed and part charred with very little melting. This behavior is similar to that of the hexamethylenetetramine *o*-cresol compound.

Hexamethylenetetramine Carvacrol.

The compound shows a point of liquefaction at 148° C., at which point it resinifies quickly.

The reaction between phenol and hexamethylenetetramine is carried out under anhydrous conditions by Goldsmith.¹⁸ The proportions of the ingredients are such as to furnish one group of phenolic body to each methylene group of the hexa. The mixture is heated, with evolution of ammonia, until a sample solidifies on cooling. The product is soluble in ordinary solvents and can be hardened and rendered infusible and insoluble by further heating under pressure. The employment of a solvent facilitates the control of the reaction and produces a more homogeneous resin. Goldsmith¹⁹ uses xylol as a solvent to moderate the reaction. If a large amount of xylol is used the resin separates during the latter part of the reaction either as a solid mass or a pulverulent precipitate. For example, 40 grams phenol, 10 grams hexa and 50 grams xylol are heated together under reflux condenser, slowly raising the temperature to about 165° C. when the product precipitates as a resinous mass and the xylol can be poured off and used again. Redman²⁰ reacts together 1 mol. of hexa with more than 5 mols. of phenol in the presence of a solvent, such as alcohol or acetone, which acts as a controlling agent and retards the reaction. By heating the mixture at 80° C. for about 5 hours he forms an initial condensation product which can be used as a coating or binder, glue or adhesive. By subjecting to further heat and pressure the product is transformed into a hard, infusible, insoluble resin. Glycerol can be added to the raw materials to make the final product more pliable and produce a ruby-red color.

The substitution of hexamethylenetetramine according to Redman, Weith and Brock²¹ overcomes a number of the difficulties which arise when aqueous formaldehyde is used. A molding composition may be prepared from hexamethylenetetramine 75 parts, dissolved in cresol 300 parts, and the solution mixed with asbestos pulp 600 parts and asbestos fibre 150 parts. Additions of pitch, asphalt or varnish resins may be made. The composition is molded by hot pressing to obtain infusible articles. Hydrobenzamide or benzaldehydeamine also may be used with phenol, cresol or xylenols.

By reacting on phenol or cresol with hexamethylenetetramine Redman^{21a} obtains soluble fusible resins which may be further treated with

¹⁸ U. S. Pat. 1,230,829, June 19, 1917.

¹⁹ U. S. Pat. 1,375,959, Apr. 26, 1921.

²⁰ U. S. Pat. 1,107,703, Aug. 18, 1914.

²¹ U. S. Pat. 1,368,753, Feb. 15, 1921; Chem. Abs. 1921, 1196.

^{21a} U. S. Pats. 1,188,014, June 20, 1916; 1,242,592, Oct. 9, 1917.

ammonia will be evolved and the mass is viscous when hot, brittle when cold. Redman has succeeded in casting in open molds mixtures made in these proportions, allowing hardening to take place by heating without application of external pressure. Transparent rods 2 feet long and $1\frac{1}{2}$ inches in diameter free from fractures and gas bubbles were obtained.

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^{17a} J. Ind. Eng. Chem. 1921, 13, 153; Hexamethylenetetramine-triphenol and phenol alcohols, see Baekeland, U. S. Pat. 1,442,420, Jan. 16, 1923.

without a catalyzer, to obtain a permanently fusible resin; drying and incorporating with hexamethylenetetramine, paraform and a basic catalyzer or any other anhydrous aldehyde compound serving to add the aldehyde necessary to bring about hardening under heat and pressure to an insoluble, infusible resin during the molding operation.

One Stage Process.

In carrying out the one stage process phenol and ordinary aqueous formaldehyde (about 37 per cent) are mixed and a catalyst, usually a small amount of ammonia, is added. The mixture is heated in a digester to a temperature around 80-90° C. When resinification has occurred the water present in the formaldehyde and liberated by the reaction is boiled off. Owing to the presence of the catalyst such a resin is liable to change considerably in fusing point during the drying and in fact may become converted to a rubbery infusible mass which has to be discarded. When a batch goes over into a rubbery mass its removal from the digester is a laborious operation. Hence the principal objection to a one stage process is the difficulty of securing uniform product. The control of the reaction becomes more and more difficult as the water is removed even though this take place *in vacuo*, and at the end of the dehydration step it is necessary either to immediately add alcohol, acetone or some other solvent with strong agitation to check the reaction by dilution or else to run off the resin and allow to cool in thin layers.

The rubbery product obtained when the reaction proceeds somewhat past the initial soluble state but not to the hard infusible state, has aroused considerable interest in the possibility of using the substance as a soft rubber substitute. Provided the material possessed the qualities of completely-reacted phenol-formaldehyde resins (e.g. indifference to solvents, oils, sunlight and aging) and in addition remained soft and rubbery, an interesting future might be predicted for it. However, the resin in this state is not sufficiently stable for commercial uses for, on exposure, it gradually hardens to a brittle mass which on further heating is converted to the final hard infusible product.

Two Stage Wet Process.

This process has found favor from a manufacturing standpoint as it gives reasonably uniform results. The initial stage is carried out without the use of a catalyst but a much higher temperature is employed than in the one stage process employing a catalyst. A temperature of between 140-165° C. may be used. The materials are charged into a jacketed steel digester which may be safely operated at pressures of 100-110 pounds. The heating is very gradual because the reaction starts at about 140° C. and proceeds quite vigorously. When the reaction begins the digester is cooled and the reaction is carefully watched by drawing samples to determine viscosity and melting point. For a charge of say one-half ton the reaction is usually complete in about 3 to 4 hours. At this high temperature the water may be elimi-

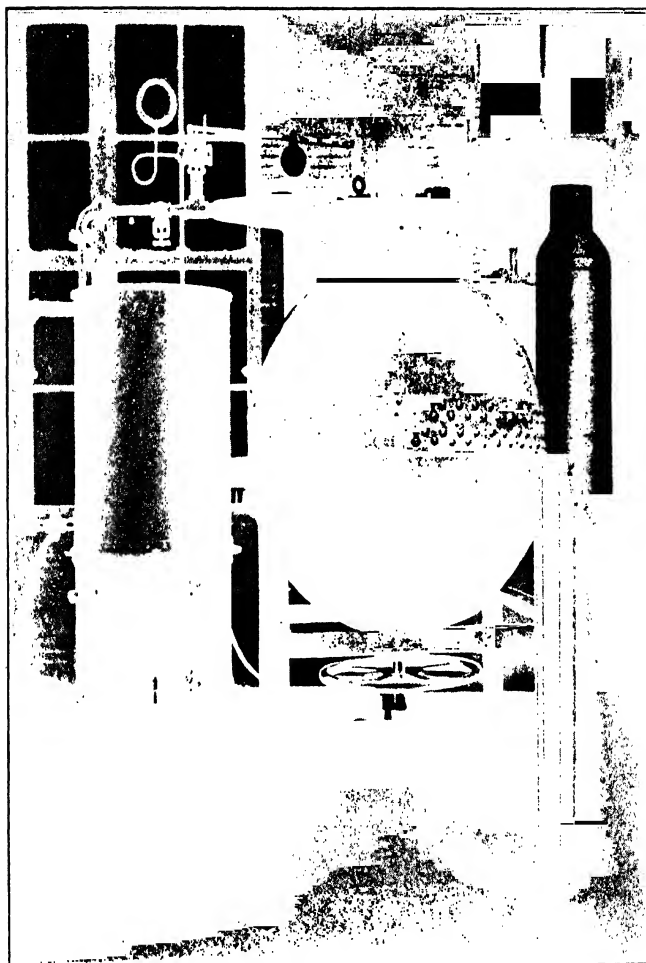
nated simply by carefully venting the digester through a valve. The entire operation of heating to the reaction point, carrying out the reaction and drying requires 15 to 18 hours. Care should be taken not to have the formaldehyde too concentrated as the reaction may be difficult to control. Formaldehyde of commercial strength ordinarily is satisfactory but varies slightly and sometimes may be stronger than is desirable in which case it may be diluted with water. It would not be possible to make fusible resin at these temperatures with paraform as the reaction would be far too violent.

The dried resin at the temperature of the digester is a thin liquid which is run into pans and allowed to cool. When hard the slabs of resin are broken into coarse fragments.^{21b}

Dry Process.

This method, as has been previously stated, is generally limited to the preparation of amber substitutes. Like the wet process it may be carried out in either one or two stages. Thus by causing hexamethylenetetramine to react with phenol in excess fusible resins are obtained. The phenol and hexa mixture may be heated in a steam jacketed kettle. This is usually closed and provided with a means of absorbing in formaldehyde the ammonia which is evolved during the reaction. In this way fresh quantities of hexa are obtained. The temperature is raised to 60-80° C., at which point the reaction starts with the evolution of large quantities of ammonia. The reaction is associated with a rise in temperature. If an excess of phenol is employed in order to produce a fusible resin the temperature can be raised safely to 140-180° C., but when the entire amount of hexa to produce an infusible resin is added at one time, a lower temperature should be maintained by circulating cold water through the jacket of the kettle. The reaction is allowed to progress with heating if necessary for a sufficient length of time to drive off most of the ammonia. This may

^{21b} The Aylsworth process on which the manufacture of Condensite is based is a two-stage process involving, first the preparation of a fusible resin, thoroughly drying it, and mixing with hexamethylenetetramine as a hardening agent. Brown, J. Ind. Eng. Chem., 1916, 1172, states that according to the principal Aylsworth process a phenol resin is first prepared in which the proportion of methylene is such that the resin is permanently fusible. It may be heated to 420° F. (216° C.) or higher. In consequence it can be heated sufficiently high to accomplish complete dehydration. Aylsworth observed that a temperature of about 400° F. (204° C.) was required to remove all the water free and combined. The dehydration of a partial condensation product of a character which becomes infusible on further heating of course could not be carried out in this manner. To form the final fusible product the dehydrated resin is combined with hexamethylenetetramine or paraform. One advantage in using hexa is that the reaction is more nearly anhydrous, ammonia being evolved but no water or formaldehyde such as would be observed in the case of paraform. Brown states no counteracting pressure is needed and that the ammonia evolved may be rendered harmless by an added substance such as an organic acid anhydride. Brown claims that Aylsworth was thus the first to form an entirely anhydrous commercial final product and that a material of this character is of great advantage where high dielectric results are desired.



Courtesy of I. O. Koven & Brother.

FIG. 4.—Digester adapted for the preparation of phenol-formaldehyde resins. It is steam jacketed and provided with a large valve at the bottom for drawing off the product. At the right is shown a superheater for steam. At the left is a condenser so constructed as to permit distillation in vacuo. The manhole at the top of the digester is an essential feature. Digestors may be made of steel and may be cylindrical instead of spherical.

require from 5 to 6 hours. If the product is a fusible resin it may be allowed to cool in large pans to a hard brittle product. In the case of a thermo-setting resin castings may be made in suitable molds or in some cases the resin while hot may be mixed with fillers.

Baekeland's Heat and Pressure Process.

Products similar to hard rubber or ivory, insoluble in alcohol and acetone, resistant to heat, moisture and most chemical reagents have been obtained by Baekeland by molding phenol-formaldehyde resins under heat and pressure.^{21c} Phenol or cresol is treated with about an equal volume of commercial formaldehyde solution, affording formaldehyde in approximately molecular proportions or a slight excess of the latter may be employed. On heating, with or without the presence of catalytic bodies, reaction takes place and a heavy oily or viscous layer separates from an aqueous solution. The aqueous layer is rejected and the oily liquid, which is soluble in alcohol and acetone, may be heated on a steam bath to thicken slightly and drive off any water which may be present in the mass. If the reaction is permitted to proceed further the product may become gelatinous. This modification is insoluble or incompletely soluble in alcohol but more readily soluble in acetone. By heating this product it is converted into a hard heat resistant body. Various fillers may be incorporated, these covering a wide range of substances such as asbestos, wood fibre, rubber, zinc oxide, barium sulphate, calcium sulphate, graphite, horn, bone, starch and pumice stone. Modifying agents, including resins, nitrocellulose and casein, may be added. On exposing the material at 110-140° C. under pressure a hard compact molded article is obtained in from 1 to 2 hours' time. Baekeland observes that various catalytic agents such as acids or salts, including zinc chloride and calcium chloride, may be employed. At the present time the use of acid condensing agents is not favored for practical molding operations on account of the danger of corrosion of the molds. The present practice also enables molding to be carried out in much less time than specified above.^{21d}

Baekeland^{21e} prepares a solid partial reaction product of phenol and formaldehyde to which may be added a filler (e.g., wood flour). The whole is comminuted, molded under pressure, and by heating at 100-200° C. transformed into an insoluble and infusible condensation product. Asbestos fibre and other fibrous or cellular materials, rubber, casein, lampblack, mica, mineral powder such as zinc oxide, barium sulphate, etc., pigments, dyes, nitrocellulose, abrasive materials, lime, calcium sulphate, graphite, cement, powdered horn or bone, pumice stone, talc, starch and resins also are suggested as fillers. Wood flour is especially useful to retard shrinkage and brittleness.

^{21c} U. S. Pat. 942,699, Dec. 7, 1909.

^{21d} This patent has been involved in litigation, United States District Court, Eastern District of New York, brought by the General Bakelite Company against the General Insulate Company, the patent being held valid as a result of such litigation.

^{21e} U. S. Pat. 939,966, Nov. 16, 1909.

With the object of producing shaped or molded articles without keeping the material in molds during the entire hardening operation Baekeland^{21f} prepares an initial condensation product from approximately equal volumes of ordinary commercial formalin and phenol or cresol. Water is separated and the oily or viscous material is subjected to gentle heating to bring about transformation into an intermediate product which is solid at all temperatures. This product is more or less hard when cold but becomes elastic when slightly heated and is capable of yielding to pressure, resuming its original shape if the pressure be discontinued. In this form the material is insoluble in alcohol and glycerol but swells in phenol and in acetone. These properties of the intermediate product are utilized by heating the initial product in molds until the intermediate product is formed. The shaped masses then may be removed from the mold and subjected to further heat treatment to bring about hardening, as heat may be applied under these conditions without danger of deformation. By this procedure the molds quickly become available for further work. The molded articles in the intermediate stage of conversion may be hardened by baking at low temperatures in the open air or in an atmosphere of an inert gas. Or the final heat treatment may be carried out under a pressure above atmospheric. The process enables the production of large blocks free from gas bubbles or pores.

Phenol Alcohol Resins.

Infusible molded articles are made by Baekeland from oxybenzyl alcohol or other phenol alcohols.^{21g} In one case phenol alcohols or their anhydrides (saliretins) and formaldehyde, with or without a condensing agent, are heated to produce hard thermo-rigid resins. In place of formaldehyde the polymers may be used. When ammonia is employed as a condensing agent hexamethylenetetramine is produced which of course serves as a hardening agent. In the infusible state the resin may be incorporated with a variety of filling materials in the same manner as is employed in making rubber compositions. Thus asbestos, wood fiber, mineral powders and pigments may be introduced. Organic substances such as naphthalene, anthracene, aniline, phenols, pitch, asphaltum, cumaron resins and other resinous bodies, paraffin and the like may be added. Another procedure is that of treating phenol alcohols or their anhydrides with basic catalysts to yield resinous substances which are less hard and less resistant to heat and to solvents than the resinous products obtained above with the aid of additional formaldehyde. Suitable catalysts are ammonia or the carbonate, caustic alkalis and their carbonates, aniline, pyridine, barium or calcium hydrates, alkali sulphides, acetates and cyanides, borax, soaps and trisodium phosphate. Fillers may be incorporated with the resinous

^{21f} U. S. Pat. 942,700, Dec. 7, 1909; German Pat. 237,790, Nov. 28, 1908.

^{21g} U. S. Pats. 1,038,475, Sept. 10, 1912; 1,146,045, July 13, 1915; 1,187,232, June 13, 1916.

material thus obtained and the composition molded under heat and pressure.

Polymers of Formaldehyde.

Aylsworth²² heats a formaldehyde compound (having the formula $(\text{CH}_2\text{O})_n$ in which the n is less than 4) at a temperature not exceeding 350° F. (177° C.) with an anhydrous fusible phenol resin, for a length of time sufficient to cause complete hardening. The proportions of the two reacting bodies are determined by ascertaining the amount of free phenol in the phenol resin and calculating the amount of formaldehyde compound necessary for complete combination to form a hard infusible resin.

The production of light-colored phenol-formaldehyde resins depends, according to Pollak, on the use of a minimum amount of condensing agent and the removal of excess phenol by washing with warm water. The use of a sensitive form of trioxymethylene (β and γ polyoxymethylene) makes the addition of a special catalyst unnecessary. A method employed by Pollak is to add anhydrous trioxymethylene (20 parts) to phenol (370 parts) and metacresol (6 parts) heated on a water bath. At 85° C. reaction sets in with the evolution of heat and the temperature rises to above 100° C. After the temperature has fallen below 100° additional trioxymethylene is added and the heating and cooling allowed to take place after each addition until 80 parts of the methylene compound have been introduced. The mass is repeatedly washed with large quantities of water at a temperature below 40° C. and is then heated to about 130° C. The resin is used as a substitute for shellac.²³ The discoloration of the resin on exposure to light and air is considered by Pollak²⁴ to be due to the presence of small amounts of leuco bases which gradually oxidize to colored substances. These may be washed out of the resin along with free phenol and the elimination of the latter yields a light-proof product. A soft resin, therefore, is prepared and this material is very thoroughly washed first with water and then with water containing methyl alcohol or acetone. In one case Pollak heats 100 parts by weight of crystallized phenol with 80 parts of 40 per cent aqueous formaldehyde in the presence of 0.2 parts of sodium phenylate. The heating is carried out under a reflux condenser until the condensation product precipitates. The heavier resinous layer is separated from the supernatant aqueous solution and is washed repeatedly with water. Then it is washed with water containing 10 per cent of methyl alcohol and finally with cold water. The residue is freed from the last traces of phenol by distillation in vacuo. When filled into molds and heated to 95-120° C. an infusible and insoluble product is obtained which is transparent, of a light yellow color and is stated to be air- and light-proof. In another case Pollak treats 94

²² U. S. Pat. 1,102,630, July 7, 1914; J. S. C. I. 1914, 931.

²³ U. S. Pat. 1,210,982, Jan. 2, 1917.

²⁴ U. S. Pats. 1,211,227, Jan. 2, 1917, and 1,369,352, Feb. 22, 1921.

parts of crystallized phenol with 15 parts of finely powdered α polyoxymethylene and a quantity of 1/5 N sulphuric acid is added sufficient to start an exothermic reaction and to cause the polyoxymethylene to dissolve. The mixture is heated to about 85° C., 5 parts additional of polyoxymethylene being added after the reaction has started and also a further quantity of the sulphuric acid solution. The soft resinous mass obtained is washed repeatedly with water and treated with a 0.3 per cent solution of hydrogen peroxide. After standing for some hours the mass is repeatedly washed with water. This material constitutes an intermediate product which when mixed with fresh formaldehyde or polyoxymethylene can be converted into a light- and air-proof insoluble product.²⁵

Gaseous Formaldehyde.

The treatment of phenol with gaseous formaldehyde has been proposed by Aylsworth.²⁶ Formaldehyde gas is introduced into an autoclave containing phenol or cresol maintained at a temperature of 260-340° F. (127-171° C.). Pressure is maintained slightly in excess of the vapor tension of the mixture by feeding compressed formaldehyde gas into the autoclave as rapidly as it combines with the phenol. When the pressure is raised to 50-100 lbs. per square inch very good results are obtained. The contents of the autoclave are agitated during the gassing treatment. The operation is continued until a sample shows 12 per cent or less of free phenol. The resulting resinous product is dehydrated at 400° F. (204° C.) and is cast into slabs for subsequent use.

Other Methods Using Hexa.

Kendall²⁷ prepares a liquid mixture of phenol, formaldehyde, and water containing dissolved hexamethylenetetramine in which the formaldehyde is present in sufficient quantity to react with the phenol to form a fusible resin, and the hexamethylenetetramine sufficient to react with the resin to form an infusible product. The mixture is heated to cause reaction between the phenol, formaldehyde, and hexamethylenetetramine and obtain a fusible resin containing hexamethylenetetramine in solution but substantially no uncombined formaldehyde.

By dissolving a fusible phenol-formaldehyde resin in alcohol and adding hexamethylenetetramine a lacquer or varnish is obtained by Aylsworth²⁸ which may be transformed into a hard, insoluble and infusible product by evaporating the solvent and heating the residue. The resin and hexa may be mixed in a dry state and marketed in this

²⁵ J. S. C. I. 1915, 1154; 1916, 1226; Chem. Abs. 1914, 434; 1917, 877, 2050; 1921, 1381; British Pat. 18,281, 1912; 20,977, 1914; 14,490, 1915; Swiss Pat. 73,579, 1916; Swedish Pat. 41,636.

²⁶ U. S. Pat. 1,029,737, June 18, 1912.

²⁷ U. S. Pat. 1,418,718; June 6, 1922; J. S. C. I. 1922, 41, 558A.

²⁸ U. S. Pats. 1,098,608, June 2, 1914; 1,137,374, Apr. 27, 1915.

form. Naphthalene, nitro and chlornaphthalenes may be added as plasticizing or softening agents. A lacquer²⁹ also is made from fusible resin containing free phenol up to about 20 per cent. To this is added paraform or hexa sufficient in quantity to form an infusible product when exposed to heat. Acetylene tetrachloride or a mixture of alcohol and the tetrachloride may be used as a solvent. It may be noted that solutions of fusible phenol-formaldehyde resins in alcohol admixed with hexamethylenetetramine are not stable and especially when allowed to stand in a warm situation will increase in viscosity in the course of a few days, becoming gelatinous and finally an insoluble resin precipitating. Therefore while hexa is useful as an addition to varnish which is to be employed immediately in the impregnation of wood flour or other filler it is not well adapted for making varnishes and lacquers which are required to have good keeping qualities. Paraform or some other anhydrous polymer of formaldehyde may be used without a condensing agent. Lacquers made from phenol-acetaldehyde resin exhibit a greater degree of stability in the presence of hexa than those produced from formaldehyde.

To avoid the thickening and deterioration of solutions containing reactive phenol-formaldehyde resins, Redman, Weith and Brock³⁰ prepare a solution of non-reactive soluble phenol resin in a solvent such as alcohol and add, immediately prior to use, an alcohol and water solution of hexa, in sufficient proportion to harden.

Aylsworth^{30a} also produced a hard infusible product from a resinous fusible condensation product of phenol and formaldehyde and a methylene-amine compound (e.g., hexamethylenetetramine), the mixture being heated sufficiently to cause reaction at about 200-240° F. (93-116° C.). The hexamethylenetetramine is used in a quantity at least sufficient to combine with all the fusible condensation product and free phenol contained in it. The fusible condensation product is usually dehydrated and contains no free formaldehyde. The fusible resin may contain 3 molecular parts of phenol to 2 molecular parts of formaldehyde or equivalent, to which 7.6 to 12 per cent of hexamethylenetetramine is added.

Other Methods.

A method of making a fusible resin from one which has been transformed into an infusible product has been developed by Aylsworth.^{30b} An infusible porous mass first is obtained by heating phenol, formaldehyde (40 per cent) and a small amount of either an acid or a basic catalyst. The reaction is allowed to go to completion. The porous mass is ground and baked at 350° F. (177° C.) to remove entrapped water and acid vapors. The product is heated for several hours at

²⁹ U. S. Pat. 1,102,632, July 7, 1914.

³⁰ U. S. Pat. 1,261,615, Apr. 2, 1918.

^{30a} J. S. C. I. 1912, 347; British Pat. 3496, 1911; U. S. Pat. 1,020,593; also French Pat. 436,192, 1911.

^{30b} U. S. Pat. 1,027,794, May 28, 1912.

450-550° F. (232-288° C.) in a closed vessel with approximately one-half its weight of phenol or cresol. By this treatment the resin is dissolved and converted into a fusible product possibly similar to that prepared by the preceding method. Any excess of phenol may be removed by distillation or the mass may be treated with formaldehyde gas according to the procedure outlined above. A mixture of phenol and naphthalene as a solvent may be substituted for phenol or cresol. In this case the naphthalene is removed by distillation. The foregoing method can be used advantageously to reclaim discarded or imperfect articles or scrap containing an infusible resin binder.

Absence of Catalyst.

Another method proposed by Aylsworth^{30c} involves forming a fusible phenol-formaldehyde resin without the aid of a catalyst. The ingredients, for example, 1000 parts by weight of phenol and 750 parts of a 35 per cent formaldehyde solution, are heated in a closed vessel at 300-320° F. (149-160° C.) without any condensing agent. In fact Aylsworth states that any impurity which will act as an accelerator or catalytic agent should be eliminated. Iron and lead vessels are not suitable. Iron which is well enameled or tinned and also tinned copper or nickel do not have an objectionable action. Phenol or cresol should be refined to eliminate basic metallic impurities as well as mineral acids.

Retardation of Hardening.

The observation has been made by Baekeland^{30d} that the initial resinous condensation product of phenol and formaldehyde when undiluted may be hardened to the infusible condition at temperatures as low as 70° C. When, however, alcohol is added the resulting solution may be boiled under a reflux condenser for a long time without noticeable hardening. If the amount of alcohol is large the boiling may be continued for days without bringing about the transformation to an infusible product. Baekeland finds that water does not exert a retarding effect. He makes use of this observation as follows: An initial product is obtained by boiling together phenol or cresol and formaldehyde in the presence of a basic, neutral or acid catalyst. When the reaction progresses to the point that separation of the initial product occurs the resinous material thus obtained is dissolved in an aqueous solution of sodium hydroxide. Thus 100 parts phenol, 90 parts formalin and one-half part caustic soda are boiled for 2 hours or until the liquid separates into two layers. After cooling there is added an amount of a 4 per cent aqueous solution of caustic soda sufficient to dissolve the resin. So prepared the solution keeps well but acquires a reddish color on standing. On heating to 80° C. the solution gelatinizes and on further heating hardens rapidly, yielding a transparent infusible resin. The solution may be used as a varnish or protective

^{30c} U. S. Pat. 1,102,630, July 7, 1914.

^{30d} U. S. Pat. 1,085,100, Jan. 27, 1914.

coating and for this purpose if desired may be mixed with asbestos or other fillers. In proper proportions with appropriate fillers molding compositions may be obtained.

Amber Substitutes.

The production of amber-like products, according to Redman, Weith and Brock,²⁰ is carried out by first forming an initial product from phenol and formaldehyde without the addition of any condensing agent. Thus 3 parts of a 40 per cent solution of formaldehyde and 5 parts of phenol are boiled at atmospheric pressure for a period ranging from 60 to 120 hours. A viscous creamy lower layer forms and a supernatant layer of water which is practically free from formaldehyde. Cresol does not require boiling for so long a period, ordinary commercial cresol reacting sufficiently in from 4 to 12 hours and when crude cresol is used the period may be shortened to about 2 hours. With pure phenol the reaction may be accelerated by heating under pressure to 125° C. In this case the time of heating will range from 12 to 18 hours. After a viscous resinous mass is obtained in this manner 2 parts additional of formaldehyde, that is, two-thirds of the amount of formaldehyde originally employed, is stirred into the first reaction product (the water which separated in the first stage having previously been removed). The formaldehyde is added at a temperature of about 100° C. and the mixture allowed to cool to 60-70° C. Then heat is applied and water is evaporated rapidly, the temperature rising to about 115° C. Some formaldehyde will escape during this operation. Ordinarily the concentration is carried to a point which renders the mix quite viscous but still permits pouring. Boiling should be stopped before the material reaches a gelatinous state. After concentration 3 to 5 per cent of formaldehyde is added to replace loss occurring during concentration and the material is poured into molds. It is allowed to set at a temperature of 50-100° C. When sufficiently firm it is removed from the molds and kept at the same temperature for a period of several weeks or several months, depending on the thickness of the molded masses. By mildly heating the material for a protracted period as described, an amber-like product is obtained which is used to make pipe stems, cigar holders and similar articles. A finer color may be obtained and a harder product which may be machined, sandpapered and buffed to better advantage by exposing the material to a finishing heat of 125° C. or even higher for a period of several days. The color may be varied by introducing dyes such as auramin to produce a deep amber color or methyl violet to yield an amethyst color. The addition of oils or waxes in small quantity yields an opaque material. Ground mica or fish-scales may be used to produce a shimmering effect.

Backeland²¹ prepares amber-like products by heating phenol and hexamethylenetetramine, with or without the presence of water, to form hard, infusible resins containing free ammonia.

Uniting Resinous Masses.

Sections of infusible and substantially insoluble resinous phenol-formaldehyde condensation products may be united according to Redman, Weith and Brock²⁰ by softening the faces to be joined through the action of a liquid such as acetone or alcohol, coating the surface with a fusible phenol-formaldehyde resin and heating the faces pressed together until the intervening film becomes infusible.

²⁰ J. S. C. I. 1919, 647A; U. S. Pats. 1,310,087 and 1,310,088, July 15, 1919; 1,374,526, Apr. 12, 1921.

²¹ U. S. Pat. 1,187,230, June 13, 1916.

²² U. S. Pat. 1,424,738, Aug. 1, 1922.

450-550° F. (232-288° C.) in a closed vessel with approximately one-half its weight of phenol or cresol. By this treatment the resin is dissolved and converted into a fusible product possibly similar to that prepared by the preceding method. Any excess of phenol may be removed by distillation or the mass may be treated with formaldehyde gas according to the procedure outlined above. A mixture of phenol and naphthalene as a solvent may be substituted for phenol or cresol. In this case the naphthalene is removed by distillation. The foregoing method can be used advantageously to reclaim discarded or imperfect articles or scrap containing an infusible resin binder.

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Another method proposed by Aylsworth^{30c} involves forming a fusible phenol-formaldehyde resin without the aid of a catalyst. The ingredients, for example, 1000 parts by weight of phenol and 750 parts of a 35 per cent formaldehyde solution, are heated in a closed vessel at 300-320° F. (149-160° C.) without any condensing agent. In fact Aylsworth states that any impurity which will act as an accelerator or catalytic agent should be eliminated. Iron and lead vessels are not suitable. Iron which is well enameled or tinned and also tinned copper or nickel do not have an objectionable action. Phenol or cresol should be refined to eliminate basic metallic impurities as well as mineral acids.

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The observation has been made by Baekeland^{30d} that the initial resinous condensation product of phenol and formaldehyde when undiluted may be hardened to the infusible condition at temperatures as low as 70° C. When, however, alcohol is added the resulting solution may be boiled under a reflux condenser for a long time without noticeable hardening. If the amount of alcohol is large the boiling may be continued for days without bringing about the transformation to an infusible product. Baekeland finds that water does not exert a retarding effect. He makes use of this observation as follows: An initial product is obtained by boiling together phenol or cresol and formaldehyde in the presence of a basic, neutral or acid catalyst. When the reaction progresses to the point that separation of the initial product occurs the resinous material thus obtained is dissolved in an aqueous solution of sodium hydroxide. Thus 100 parts phenol, 90 parts formalin and one-half part caustic soda are boiled for 2 hours or until the liquid separates into two layers. After cooling there is added an amount of a 4 per cent aqueous solution of caustic soda sufficient to dissolve the resin. So prepared the solution keeps well but acquires a reddish color on standing. On heating to 80° C. the solution gelatinizes and on further heating hardens rapidly, yielding a transparent infusible resin. The solution may be used as a varnish or protective

^{30c} U. S. Pat. 1,102,630, July 7, 1914.

^{30d} U. S. Pat. 1,085,100, Jan. 27, 1914.

a hard resin, varying in color from yellow to light brown, and melting at about 110° to 128° C. It is soluble in methyl and ethyl alcohols, dilute caustic alkali solutions, acetone, ether, carbon disulphide and chloroform; less soluble in benzol, dichlorhydrin, carbon tetrachloride, turpentine oil and fatty oils. It serves as a substitute for shellac and yields varnishes which dry well on wood or metal. The hardness of the product depends upon the proportion of formaldehyde used. Gentsch³² prepares a resin from orthocresol and formaldehyde which is claimed to be suitable for use as a varnish or polish. Hydrochloric acid is used as a catalyst and the temperature of reaction is 100° C. The resin is spirit-soluble but is insoluble in oils. Its melting point is 110 - 120° C. Baekeland³³ employs ortho and paracresol or mixtures of these as plasticizing agents for phenol-formaldehyde resins utilized in molding compositions. The cresols may be added directly to the phenol-formaldehyde resin or they may be condensed with active methylene-containing bodies to form fusible resins prior to admixture with the phenol resin. The proportion of formaldehyde may be varied considerably without changing the properties of the fusible resin very materially. A paracresol resin is obtained by heating in an open vessel 100 parts of this cresol with 45 parts of hexamethylenetetramine at 180 - 200° C. until a portion of the ammonia has been driven off. The mixture is then heated for 24 hours at about 165° C., ordinarily under pressure. (See also Blumer, Wetter, Knoll & Co., Chap. 6.)

Both ortho- and para-cresol are far less reactive than metacresol with formaldehyde and other aldehydes. The tendency is to form permanently fusible and soluble resins of the saliretin type. Orthocresol particularly is considered undesirable in making resins for molding compositions which have to be hardened in the mold. Baekeland, however, seeks to utilize this relative inactivity in the production of resins which can be used as plasticizing agents.³⁴ While it is true that infusible products may be obtained from ortho- and para-cresol their production involves a length of heating which would be out of the question in any commercial molding operation requiring hot pressing.

An infusible product may be prepared according to Baekeland when paracresol reacts upon formaldehyde present in sufficient proportions, provided caustic soda is used as the condensing agent. If hydrochloric acid is used the product is more or less fusible and brittle even when relatively large proportions of formaldehyde are used. Similar proportions reacting on phenol or metacresol would produce infusible products. Baekeland has prepared a series of resins from orthocresol which are used to retard the moment of final hardening in molding compositions made essentially of phenol or metacresol formaldehyde resins. He also describes methods of making several species of infusible resin from orthocresol as follows: 100 grams orthocresol, 64 grams formaldehyde solution (40 per cent) and 1.6 cc. strong aqueous hydrochloric acid are boiled for about 2 hours, then evaporated and heated to 200° C. A fusible resin of the saliretin type results. This is mixed with about 7-15 per cent by weight

³² U. S. Pat. 924,449, June 8, 1909.

³³ U. S. Pat. 1,306,681, June 17, 1919.

³⁴ U. S. Pat. 1,401,953, Jan. 3, 1922.

of paraform and heated for 24-48 hours in a mold heated by a steam pressure of 45-90 pounds. The product is hard and infusible. 100 grams orthocresol, 150 grams formaldehyde solution (40 per cent) and 2.5 cc. strong hydrochloric acid are boiled for 50 minutes and the reaction product heated under 60 pounds steam pressure for 10 hours. The product is infusible and tough. 100 grams orthocresol, 90 grams formaldehyde solution and 8 cc. concentrated aqueous ammonia are boiled for 11 hours and then heated under 90 pounds steam pressure for 10-14 hours. An infusible hard product results. 100 grams orthocresol, 80 grams formaldehyde solution and 5 grams of caustic soda boiled for one-half hour and heated under pressure as above yields a hard infusible mass. 100 grams of orthocresol and 40 grams hexamethylenetetramine heated to 200° C., then placed in a closed vessel and heated for 24 hours under 90 pounds steam pressure yields a product which is tough but still fusible. A hard tough product is obtained by heating 100 parts by weight of paracresol with 45 parts of hexamethylenetetramine in an open vessel at 180-200° C. until a portion only of the ammonia has been driven off, then cooling somewhat and pouring the liquid mass into a condenser. Heat is applied at 165° C. for about 24 hours. A fusible resin results.

Aylsworth³⁵ prepared an oil-soluble cresol resin by heating together ortho cresol 30 parts and a 40 per cent solution of formaldehyde, 14 to 16 parts, with a small amount of water. The water is not necessary but may amount to as much as 8 parts. The heating is done in an autoclave at 270° F. (132° C.). The purpose of the water is to decrease the violence of reaction. Excess of cresol and water are removed by vacuum distillation. The resulting resin melts at from 140-170° F. (60-77° C.) and contains under 4 per cent of cresol. The formaldehyde is all combined and the resin is soluble in varnish, oils and solvents.

Other Cresols.

Robinson-Bindley, Weller and Dulcken³⁶ prepare an oil-soluble product by condensing 50 parts of paracresol with 70 parts of formaldehyde solution of 40 per cent strength. Five parts of hydrochloric acid of 30 per cent strength constitutes the catalyst. Oil soluble resinous condensation products also are obtained from lignite tar oils or low temperature tar oils containing phenol by condensation with not more than a molecular proportion of acetaldehyde or its polymers or higher aldehydes. Mixtures of acetaldehyde and higher aldehydes likewise may be used.³⁷ The addition of these oil-soluble resins to phenol-formaldehyde resins which are insoluble in oil is stated to confer solubility upon the phenol-formaldehyde resins. Subsequent treatment of the oil-soluble resins with formaldehyde converts them into products which are insoluble in oil.³⁸

Baekeland³⁹ has produced a resin from meta cresol and formaldehyde. This may be used alone or together with a condensation product of formaldehyde and phenol, with or without a filling material, and containing corresponding

³⁵ U. S. Pat. 1,111,287.

³⁶ British Pat. 134,563, Feb. 27, 1918; J. S. C. I. 1920, 35A.

³⁷ Chemische Fabriken Worms Akt.-Ges. Brit. Pat. 156,740, 1921; Chem. Abs. 1921, 1821.

³⁸ Concerning the effect of natural resins in conferring solubility in oil, see Chapter 8.

³⁹ J. S. C. I. 1914, 430; U. S. Pats. 1,088,677 and 1,088,678, March 3, 1914.

condensation products of ortho and para cresol in minor proportions. The product may contain as essential constituents the condensation products of formaldehyde and meta and para-cresol respectively (the former in major proportions), with or without a filling material; or a mixture of phenol and meta cresol containing minor proportions of ortho and para cresol.

By boiling commercial cresylic acid of 97-99 per cent purity with such a proportion of 40 per cent formaldehyde solution that the mixture contains more than one molecule of formaldehyde for each molecule of cresylic acid and continuing the boiling until the solids determined at a temperature of 110° C. equal at least 40 per cent of the product, Handy⁴⁰ produces a resin which is infusible, hard, tough and insoluble in acetone. The final boiling during which water and formaldehyde are distilled off is conducted at a temperature of 110-120° C. The product obtained by this method is suitable for use as a binder in making brushes and for various other purposes.

A paint or enamel is prepared by Ornstein⁴¹ as follows: A solution of cresol 100, sodium hydrate 6, water 94, and 40 per cent formaldehyde 75, after standing 12 hours, is mixed with a 10 per cent hydrochloric acid solution 100 parts, and the product allowed to settle to obtain an oily layer. A second solution of cresol 100, sodium hydrate 6, water 94 and 40 per cent formaldehyde 60 parts, is heated to boiling and 15 parts formaldehyde and a 10 per cent hydrochloric acid solution are added, also forming an oily layer. The two products are mixed with solvents and pigments, to form a paint. A small quantity of a chloride, nitrate or sulphate may be added to promote hardening.

Berend⁴² produces soluble and fusible resins by condensing crude cresol containing meta cresol, or a mixture of para cresol and meta cresol, with formaldehyde and expelling and recovering the unused cresol from the product.

Transparent condensation products from a mixture of equimolecular quantities of purified cresol or phenol and (40 per cent) aqueous formaldehyde with at most 0.5 per cent fixed alkali hydroxide as catalyst are prepared by distilling off, under normal pressure, all the water used for solution and half the water formed in the condensation. To the residue is added 20 volumes (of the original volume) of methyl or ethyl alcohol. This is then mixed and half the alcohol distilled off. Subsequently the residue is poured into molds and these are dried in a drying chamber through which passes a current of air. The drying is begun at 60° and is gradually increased to 115 or 120° or higher. A hardened and non-fusible product is formed.⁴³

Resinous products suitable for the manufacture of varnishes are prepared by treating phenol alkyl ethers substituted in the meta position to the alkoxy group by an alkyl or alkoxy group, e.g., m-cresol methyl ether or resorcinol diethyl ether, or, *ar*-tetrahydronaphthol alkyl ethers, with formaldehyde, or compounds capable of yielding the same, in the presence of acids. *ar*-Tetrahydronaphthol alkyl ethers are prepared by sulphonating tetrahydronaphthalene, fusing the product with alkalis, and treating the product with alkylating agents.^{43a}

Coniferous wood tar, saponified with concentrated alkalis, separated from the unsaponifiable matter and warmed with formaldehyde yields a viscous product. This is separated from the aqueous portion, washed repeatedly with water and dried. A hard, transparent, brown

⁴⁰ Chem. Abs. 1919, 13, 369; U. S. Pat. 1,287,299, Dec. 10, 1918.

⁴¹ U. S. Pat. 1,222,980, Apr. 17, 1917.

⁴² J. S. C. I. 1917, 347; U. S. Pat. 1,214,414, Jan. 30, 1917.

⁴³ Naamlooze Vennootschap Utrechtsche Chemische Industrie. Holland Pat. 3,742, Sept. 15, 1919.

^{43a} Akt.-Ges. für Anilin-Fabr., German Pats. 358,399 and 358,400, 1920, Marx, Siebert and Wesche.

resin is obtained which is soluble in solvent naphtha, and the solution is used, mixed with mineral colors, as a paint.^{43b} Lingner^{48c} condensed vegetable tar with 40 per cent formaldehyde solution by the aid of hydrochloric or sulphuric acid. The resulting solid mass was dissolved in alkali and reprecipitated by dilute acids several times, then washed, dried and powdered. The product is claimed to possess all the medicinal properties of the original tar, but has the advantage of being practically odorless.

Benzyl alcohol is used by Howse^{48d} in preparing solutions of phenol-formaldehyde resins for use as varnishes, lacquers and paints. Various other solvents, nitrobenzol, nitronaphthalene, pitches, resins, rubber and the like may be added.

Phenols of Low Temperature Tar.

Glud and Breuer⁴⁴ have made an extensive study of the reaction between formaldehyde and various phenolic bodies obtained by condensing aldehydes with the phenols of coal tar derived by low temperature carbonization. Soluble, fusible resins were derived from these phenols by treatment with formaldehyde and ammonium chloride as a catalyst. Crude tar from which the most viscous compounds have been removed, particularly fractions distilling between 150-250° C. and also between 250-300° C., including the hydrocarbons that distil at these temperatures, were tested. The presence of hydrocarbons did not interfere with the reaction of resinification and could be removed from the resinous products after the reaction was completed. Various soluble, fusible, brittle resins were obtained. Interesting results were secured when the reaction was carried out with benzaldehyde and paraldehyde.

Phenol and Benzaldehyde.

50 parts ordinary phenol, 53 parts benzaldehyde and 2 parts ammonium chloride heated for 7 hours on an oil bath at 120° C. afforded a dark brown resin which was solid and odorless. It was soluble in alcohol and in boiling benzol. Coatings obtained from a spirit varnish made with this resin were somewhat soft.

Cresols and Benzaldehyde.

Cresols of low temperature tar were treated with benzaldehyde and ammonium chloride in the manner described when phenol was used. A thick viscous dark brown material resulted which was soluble in alcohol and benzol. When heated to 170° C. under a pressure of 10 atmospheres a transparent dark-red hard resin resulted which, however, was easily fusible and was soluble in alcohol and in aqueous solutions of caustic soda.

Cresols and Paraldehyde.

Cresols 50 grams, paraldehyde 66 grams and ammonium chloride 2 grams on heating for several hours yielded only 17 grams of a dark semi-solid mass soluble in alcohol and partially soluble in benzol.

^{43b} Chem. Fabr. Florsheim H. Noerdlinger, German Pat. 338,854, Nov. 12, 1919; J. S. C. I. 1921, 40, 742A.

^{48c} French Pat. 329,971, Jan. 31, 1903; J. S. C. I. 1903, 22, 1014.

^{48d} British Pat. 156,896, Oct. 13, 1919.

⁴⁴ Ges. Abhandl. z. Kenntnis d. Kohle 1919-1920, 4, 230.

Phenols of Low Temperature Tar and Formaldehyde.

Soluble products also were obtained by the following procedure. Proportions to correspond to one mol. of formaldehyde to one mol. of the phenolic body were taken. The formaldehyde was of 30 per cent strength. The mixtures were heated on an oil bath with reflux condenser and after being brought to boiling one-fifth of a mol. of ammonia in 25 per cent aqueous solution was added. The reaction generally was violent at first and then subsided to quiet boiling. In 30 minutes or a less period two layers were observed to form. The reaction mixture then was cooled with ice and the aqueous layer removed. The resinous mass was heated on a water bath until the odor of formaldehyde disappeared and a clear resinous product was obtained. This varied according to the character of the phenol from viscous masses, which could be kneaded, to solid resins. All of these were soluble in alcohol and alkalis. Proceeding in this manner from phenol 47 grams, formaldehyde solution 50 grams and ammonium hydroxide 6 cc. a light yellow hard opaque resin was obtained which on further heating became clear but was converted to a considerable extent into an alcohol-insoluble product. Prior to the step of further heating the resin was soluble in alcohol, the solution drying to a brittle coating on glass. Warming this on the water bath yielded a glossy amber-yellow coating no longer soluble in cold alcohol. Cresols and xlenol were treated with formaldehyde in the presence of ammonia catalyst and hard brittle resins were obtained.

Benzylamine.

An investigation of various types of phenolic bodies by carrying out condensation with formaldehyde in the presence of benzylamine also was made by Glud and Breuer. In this case the reaction was carried to the final stage by heating under pressure in a "bakelizer." In general the procedure employed was as follows: Proportions of phenol and formaldehyde (30 per cent strength) to correspond to one mol. each were mixed and heated to boiling under a reflux condenser. One-fifth of a mol. of benzylamine was added resulting in a violent reaction. The heating was continued for one-half to one and one-half hours, then the reaction mass was cooled with ice and the aqueous layer removed. Exposure to the heat of the water bath caused the opaque resinous material to become clear. The heat treatment in the bakelizer consisted in exposing in an atmosphere of carbon dioxide at 100° C. under a pressure of 1.5 atmospheres. The carbon dioxide was allowed to flow through the bakelizer and the exit gases were observed to smell strongly of phenol. The temperature was gradually raised and at the end of one hour reached approximately 170°. The carbon dioxide pressure was increased to 10 atmospheres and the resin heated for two hours at this pressure and temperature, finally increasing the pressure to about 15 atmospheres. When cold the products were very hard, clear glass-like resins free from bubbles, infusible and insoluble in all solvents. They were found to be indifferent to alkalis and most acids.

Ordinary phenol 47 grams, formaldehyde solution 50 grams and benzylamine 10 grams yielded 53 grams of soluble resin which on heating in the bakelizer changed from a red initial product to a light yellow final product. 27 grams cresol, 25 grams formaldehyde solution and 5 grams benzylamine yielded 31 grams of soluble resin which on exposure to heat in the bakelizer became very hard. The change from a dark to a light colored product on thus heating was very distinct. Entirely different results were obtained, however, when using xlenol, in this case 30 grams xlenol, 25 grams formaldehyde solution and 5 grams benzylamine yielded about 30 grams of fusible resin. Exposure to the drastic heat treatment in the bakelizer as previously described yielded a brittle fusible resin which was soluble in alcohol and was not very hard. 30 grams of phenols from coal tar, boiling at 190-230° C., 25 grams formaldehyde solution and 5 grams benzylamine on the other hand became very hard when heated in the bakelizer. In contrast to this 34 grams of tar phenols boiling point 230-260° C., 25 grams formaldehyde solution and 5 grams benzylamine after "bakelizing" yielded a dark opaque resin which was not hard but was fusible, brittle and soluble in alcohol and caustic soda solution. The same phenolic bodies 15

grams, treated with 12.5 grams formaldehyde solution and 0.6 grams carbonate of soda on bakelizing afforded a brittle but infusible mass. Phenols boiling at 260-300° C. employing benzylamine as a catalyst did not give an infusible insoluble final product.

Synthetic resins are produced by Anderson and Maclaurin⁴⁰ through the condensation of formaldehyde with the monohydric phenolic substances, boiling between 230° and 320° C., present in tars obtained by the low temperature distillation of coal.

Testing Resins.

Ten phenol-aldehyde resinous condensation products from different sources were submitted to tests by Fonrobert⁴¹ with a view to their evaluation as substitutes for shellac in spirit varnishes and polishes. The melting-points (incipient sintering to complete fusion) ranged from 40°-46° C. to 97°-105° C.; one sample, showing an incipient melting-point of 80° C., failed to melt completely, and, moreover, was the only one not completely soluble in alcohol. The ash content in no case exceeded 0.6 per cent. The acid values of eight samples ranged from 1.1 to 9.0, another sample showing a value of 42.6. Paleness of color was in most cases accompanied by a strong odor of cresol, the samples possessing strong odor, furthermore usually deepening in tint when the films from the alcohol solutions were maintained at 100° C. for 24 hours. Only two of the samples were free from smell of cresol at ordinary temperatures, and some of them contained a proportion of cresol sufficient to produce unpleasant effects as a result of contact of the skin of the hand with the varnished surface. Elasticity of the film, due to the presence of free cresol, was only transient, as was shown by observation of the films after submission to a rapid aging test (exposure at 100° C. for 24 hours). All the samples were much inferior to shellac in regard to hardness and elasticity. The films from the varnishes varied from a condition of sensitiveness to hand-warmth in the early stages, to brittleness after stoving at 100° C. for 24 hours, two samples, however, giving films which were fairly elastic after stoving. Fonrobert therefore regards phenol-aldehyde condensation products as poor substitutes for natural shellac.

In discussing the detection of phenol-formaldehyde resins Steinitzer⁴² states that when they are boiled with sodium hydroxide solution or heated with soda-lime, liberation of phenols results which may be identified by their color reactions. In plastic masses containing phenol-resins and starch or potato flour, the starch cannot be detected by the iodine reaction, but the product may be boiled with water and the extract tested for dextrin with Fehling's solution. The condensation products of phenol, formaldehyde, and casein also yield phenol when boiled with sodium hydroxide solution, but the sulphur derived from the casein should be removed by means of lead oxide before applying the test for the phenol. This method of testing would hardly serve to discriminate between resinous phenol formaldehyde condensation products and certain other resins of phenolic origin.⁴³

Herzog⁴⁹ observes that the quantity of phenol liberated by Steinitzer's method is small and obtains better results by distilling the powdered sample in a current of nitrogen. Filings of the sample are sifted to yield a fine powder. The latter is placed in a distilling flask with a long side outlet tube leading into an Erlenmeyer flask. The side tube is bent at right angles so as to extend nearly to the bottom of this

⁴⁰ British Pat. 183,629, May 17, 1921; J. S. C. I. 1922, 41, 772A.

⁴¹ Chem. Z., 1922, 46, 513; J. S. C. I. 1922, 41, 558A.

⁴² Kunststoffe, 1915, 5, 109; Z. angew. Chem. 1915, 28, Ref., 460; J. S. C. I. 1915, 1153.

⁴³ For the determination of phenol in the presence of hexamethylenetetramine and formaldehyde see Redman, Weith and Brock, J. Ind. Eng. Chem. 1914, 205.

⁴⁹ Z. angew. Chem. 1921, 31, Aufsatzteil 97. The reader interested in analytical methods should consult Ormandy and Craven, J. S. C. I. 1923, 18T.

receiver. The latter is stoppered and provided with an air condenser. A current of nitrogen is passed through the distilling flask. In this manner Herzog has obtained phenol in amount represented by one-fourth to one-fifth the weight of the sample.

This method yielded from the product Invelith (Pollak) 17.8 per cent phenol; Resan (Resanwerke) 20.5 per cent; Dekorit (Raschig) 24.2 per cent; Faturan (Traun) 21.7 per cent. The lower percentage of phenol obtained from Invelith is accounted for by its production according to a process employing dilute methyl alcohol for washing out free phenol. Herzog reacted on 48 parts formalin (40 per cent) with 60 parts of phenol in the presence of dimethylamine. The product was washed with water and dilute methyl alcohol. After hardening, the insoluble condensation product was subjected to dry distillation, yielding approximately 15 per cent of the phenol used originally. Herzog concludes that 80-85 per cent of the phenol is firmly held in combination even on heating to the carbonization point, and about 15 per cent in looser combination probably as a phenyl ether, $-\text{O.C}_6\text{H}_5$.

CATALYTIC AGENTS.

The reaction between phenol and formaldehyde, in so far as condensation is involved is initiated or accelerated by acid and basic substances. As may be expected strong mineral acids and caustic alkalis in general are the most vigorous catalysts, but for many purposes such substances are not compatible with the uses to which the final product is to be put. Both strongly basic and acidic catalysts when used in large proportions affect metals, cause deterioration of fillers and attract moisture, thus lowering the dielectric properties of the composition. Weaker mineral acids, organic acids, acid and basic salts also have been recommended. Ammonia and ammonium compounds, ammonium derivatives, hydrazine and various amines, such as aniline and benzylamine likewise have been proposed and some of these find application in commercial operations. Ammonia and certain of the amines are most favored as no objectionable degree of acidity or alkalinity remains in the final product. When ammonia is employed, as may be expected, it reacts with formaldehyde to yield hexamethylenetetramine and as this in turn reacts with phenol, ammonia is set free. Although ammonia is less objectionable than fixed alkalis as a permanent constituent of artificial amber and molded articles some means of neutralizing and fixing it would be desirable. Molded articles containing a considerable amount of ammonia are likely to blister when heated to temperatures at which the resin binder itself would otherwise be unimpaired. Aylsworth has proposed the addition of phthalic anhydride or other organic acid anhydrides as means of neutralizing free ammonia.

In a one-stage process, such as that previously described in the present chapter, the employment of basic catalysts which can be readily eliminated on heating, or can remain in the final product without harmful effect, is necessary. Mild acids can be used for limited purposes but are not as satisfactory as basic substances. The use of ammonia or its derivatives as a catalytic agent is practically universal in actual manufacturing operations.

In the two-stage process the variety of available catalysts is not so limited. Here one may employ either acid or alkaline catalysts to carry out the initial reaction or primary resinification and if such a catalyst is one which would be objectionable in the finished product because of its corrosive or hygroscopic properties its removal may be effected by neutralization or washing. However, in the final reactions yielding infusible resins a basic or mild catalyst should be used. Hexamethylenetetramine has proved useful as a finishing catalyst because it contains methylene groups which react without the evolution of water. The principal objections raised against it are that it is a water-soluble substance and any excess of it is deleterious and that it liberates ammonia which causes blistering. As stated, an improved product doubtless could be made if some means were found for completely fixing any ammonia thus developed. Baekeland and others have endeavored to meet the objection against hexamethylenetetramine by employing compounds of formaldehyde and amines such as anhydroformaldehyde aniline. It may be noted that the products of reaction of ammonia with acetaldehyde and furfural are distinctly different in their properties from hexamethylenetetramine.

In the following pages a review appears of the numerous suggestions offered in this phase of manufacturing phenol-aldehyde resins and molding compositions. In addition to this review the reader should refer to the preceding portion of this chapter and to Chapter 6 where mention has been made of other catalysts and methods of application. The processes of manufacturing these resins and the catalysts employed are so inter-related that any attempt to separately classify these is not without attendant difficulties.

Baekeland condenses phenol⁵⁰ with formaldehyde in the presence of a base such as ammonia, ammonium carbonate, caustic alkalis or carbonates, aniline, pyridine, amines, or salts which by secondary reaction engender bases, as, for instance, alkali sulphites or sulphides, acetates and cyanides, sodium triphosphate, borax and soaps. The quantity of base does not exceed one-fifth of the amount required to form the phenolate.⁵¹ Baekeland⁵² also has used larger proportions of base than specified above, but in this event partially neutralizes, with an acid or acid salt, to reduce the basic condensing agent to $\frac{1}{2}$ or less of the equivalent proportion of phenol used. As an example, 100 grams phenol are dissolved in an aqueous solution containing 50 grams caustic soda and reacted with 100 cc. of 40 per cent formaldehyde. Addition of an acid, such as sulphuric or hydrochloric acids, precipitates the partial condensation products which may be washed to eliminate water-soluble salts.

Aylsworth⁵³ has condensed phenol and formaldehyde in the presence of a base; subsequently converting the base into an electrically insulating salt which may be left in the final product without impairing the dielectric properties. Ammonia, or its basic derivatives, caustic alkalis or carbonates or alkaline earth hydroxides or oxides, such as calcium strontium or barium hydrates, are used. Organic acids, such as palmitic or stearic acid, or an acid resin, such as colophony, are considered of value to neutralize ammonia, etc., but for alkaline

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⁵¹ J. S. C. I. 1909, 374; British Pat. 21,566, Oct. 12, 1908.

⁵² U. S. Pat. 1,187,229, June 13, 1916.

⁵³ U. S. Pat. 1,146,300, July 13, 1915.

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⁵² U. S. Pat. 1,187,229, June 13, 1916.

⁵³ U. S. Pat. 1,146,300, July 13, 1915.

the accelerator is not added until the second reaction (i.e., during the baking), the product will be transparent. If desired, pigments may be incorporated with the material, or small proportions of glycerol, paraffin, gums, resins, etc., may be introduced.

Transparent resinous products are obtained by Van Voorhout⁶⁵⁰ in the following manner. Equal quantities of phenol and formaldehyde solution (40 per cent) are mixed and heated in the presence of 0.5 per cent potassium hydroxide. The heating is carried out in a steam-jacketed vessel under continual stirring until all of the water originally present and about one-half of the amount of water formed by the reaction has been removed by distillation. The mass then begins to foam strongly and at this point the steam is shut off and 20 per cent by volume of ethyl or methyl alcohol is introduced. This addition prevents the reaction proceeding too vigorously. One-half of the added alcohol is removed by distillation and the mass is cast into molds. These are placed in drying chambers at a temperature initially of 60° C. The drying is effected in three periods of about 10 hours each; during the first period a temperature of 60° C. being attained, during the second period 80° C., and finally the temperature being raised to 115-120° C. The molds have an opening at the top and during the drying process the alcohol and water escape. The final hardening takes place only after substantially all volatile substances have evaporated. Opaque products are made from cresol and formaldehyde in a similar manner, a small amount of turpentine, glycerol and vaseline being added. In this case the final temperature is 180° C.

Matsumoto⁶⁵¹ obtained the best results, as regards yield and quality of product, by the use of sodium hydroxide and ammonia as condensing and hardening agent respectively. Sulphuric acid, hydrochloric acid, ammonia, hexamethylenetetramine, aniline, sodium sulphite, and sodium carbonate were also satisfactory as condensing agents, but only basic substances such as alkali hydroxides or ammonia were found to be suitable as hardening agents.

Products⁶⁵² intended for plastic purposes are obtained by the condensation of formaldehyde or substances yielding it, with o-, m-, or p-cresol, in the presence of an inorganic fixed base or an alkali salt, e.g., sodium hydroxide or sodium carbonate, sodium alcoholate or sodium formate. In using sodium carbonate as a catalyst the interesting observation is made by Lebach⁶⁵³ that carbon dioxide is expelled violently after a short heating and presumably the caustic alkali set free is effective in carrying out the condensation. Regal has prepared an insulating material⁶⁵⁴ by heating a mixture of phenol 2 parts, formaldehyde 1 part, sodium carbonate 0.2 part, and soluble glass 0.5 to 1 part, on a water-bath until homogeneous, then heating the product in hot water and allowing it

⁶⁵⁰ U. S. Pats. 1,271,392 and 1,271,393, July 2, 1918; French Pat. 483,417, July 4, 1917; Chem. Abs. 1922, 4023.

⁶⁵¹ J. Chem. Ind. (Japan), 18, No. 207; Chem. News 1915, 112, 195; J. S. C. I. 1915, 1104.

⁶⁵² Robinson-Bindley, Weller and Dulcken, Chem. Abs. 1920, 3134; British Pat. 145,128, 1919.

⁶⁵³ J. S. C. I. 1913, 32, 559.

⁶⁵⁴ J. S. C. I. 1914, 974; French Pat. 468,241, Feb. 9, 1914; Chem. Abs. 1918, 412; Holland Pat. 2,187, 1917.

to settle in cold water. Sodium aluminate or zincate or aluminum acetate may be employed instead of soluble glass, each of these salts acting as a condensing agent, and being at the same time decomposed into acid and base, precipitating mineral matter throughout the mass. A phenol-formaldehyde resinous product of low viscosity and high solubility is obtained by Aichtmeyer⁶⁸ by the use of sodium tungstate as a catalyst.

Carbides, Nitrides, Cyanamides, etc.

Metal carbides,⁶⁹ nitrides, cyanamides, silicides or phosphides are used by Nuttall to complete condensation. When such bodies are used only for completion of the process, the initial stage of the condensation may be carried out with aqueous formaldehyde by the usual methods, the layer of condensation product separated from the aqueous layer and then treated with the specified condensing agents. Phenol, paraformaldehyde and calcium carbide; cresol, paraformaldehyde and calcium cyanamide or aluminum nitride may be used. Cresol condensed with aqueous formaldehyde in the presence of ammonium chloride yields a resin which is treated with calcium carbide. The insoluble infusible products finally obtained are water-free and have high insulating properties.⁷⁰

Jaloustre, Kheifetz and Warchavsky⁷¹ produce an acid-resistant infusible resin by reacting on phenol with formaldehyde of 40 per cent strength in the presence of sodium salicylate or ammonium thiocyanate 5 per cent, and sodium cyanide 2 per cent of the weight of the phenol. A liquid and soluble product is obtained which is heated to 95-100° C. in an open vessel. 100 parts of phenol, 160-180 parts formalin solution and 10 parts of slaked lime or 5 parts potassium cyanide also yield resins which are converted into the final infusible form on heating to 90-120° C. for 4-6 hours.

Sodium Glycerate.

Heinemann⁷² considers the addition of a small amount of sodium glycerate to improve the quality of phenol-formaldehyde resins.

Calcium Cresylate.

Brown and Kendall⁷³ make use of trioxymethylene or other equivalent active methylene-containing substances in proportions which are capable of yielding a final infusible and insoluble product. The mixture is placed in a vessel having a relatively large cooling surface and heated sufficiently to start the reaction and the latter is then allowed to proceed, under its own developed heat, until evolution of heat ceases and an intermediate product, liquid at room temperature, is formed. This product may be rendered insoluble and infusible by further heating. Calcium cresylate has been found a good condensing agent. It is prepared by heating together lime and cresylic acid in equimolecular proportions, stirring and permitting the water formed by the reaction to escape. The product is compressed into the shape of balls and is suspended in wire cages in the reaction chamber. Phenol and trioxymethylene, the latter present in a proportion somewhat greater than equimolecular are heated to 60-70° C. to start the exothermic reaction. This is allowed to progress spontaneously, the temperature being held at about 70° C. by cooling the reaction mixture. The liquid resin will harden to a final infusible and insoluble product by heating for 5 to 6 hours at a temperature between 80-100° C. The exothermic reaction also

⁶⁸ U. S. Pat. 1,429,265, Sept. 19, 1922.

⁶⁹ Chem. Met. Eng. 1921, 796; J. S. C. I. 1921, 91A; British Pat. 154,656, 1919.

⁷⁰ The provisional specifications are not confined to the specific condensing agents mentioned above, and refer also to the use of sodamide, metal alcoholates and the compounds of ammonia with zinc or calcium chloride.

⁷¹ J. S. C. I. 1921, 122A; British Pats. 138,061 and 139,147, 1919.

⁷² Chem. Age, London, 1922, 7, 461; U. S. Pat. 1,441,981, Jan. 9, 1923; British Pat. 184,984, 1921; Chem. Abs. 1923, 218.

⁷³ Chem. Abs. 1918, 1590; U. S. Pat. 1,263,031, April 16, 1918.

may be carried out without the use of any catalyzer but in this case the initial temperature should be about 88° C. as the reaction progresses more sluggishly than when catalyzers are present.

Sulphonated Compounds.

Tarasoff and Shestakoff¹⁴ produce solid, infusible, and insoluble products by condensing phenols with formaldehyde in presence of ammonium, alkali, or alkaline-earth salts of sulpho-acids (the so-called sulpho-aromatic fatty acids which are formed by sulphonating mixtures of fatty oils or olein with aromatic hydrocarbons) and of an acid which does not decompose such salts. For example, 300 parts by weight of cresol are gradually mixed with 135 parts of a 40 per cent solution of sodium salts of "naphtha sulpho-acids," 9 parts of hydrochloric acid (specific gravity 1.14), and 150 parts of 40 per cent aqueous formaldehyde, and heated to 65-70° C. A resinous liquid mass separates with a watery layer on top; the latter is removed and the resinous mass heated until there is a loss of 70-75 parts by weight of the total materials used. After cooling to 35-45° C. 120 parts by weight of aqueous 40 per cent formaldehyde are added and the whole mixed to a homogeneous mobile liquid, which is poured into molds, cooled, then gradually heated for one hour to 45° C., then, at intervals, by 10°-15° at a time, to 100° C.

Pollak¹⁵ uses crystallized phenol 18.8 parts, paraformaldehyde 8.73 parts and an aqueous solution of p-phenolsulfonic acid 0.04 part. The mixture is warmed on a water bath and after completion of the reaction, which ensues with a slight further rise of temperature, the product is poured into molds in which it becomes hard and insoluble at about 100° C. As an alternative method, phenol 100 parts, 40 per cent formaldehyde solution 125 parts, and hydrochloric acid (sp. gr. 1.19) 0.30 parts are evaporated and stirred on a water bath. When about 60 parts of the mixture have evaporated, reaction sets in with sufficient vigor to raise the temperature to above 100° C. and after some time a white precipitate separates from the clear solution. There is added about 30 parts of water and this is evaporated at about 75° C. The mass is then poured into molds heated to 70-80° C. and forms a solid which is elastic when warm. When the temperature is raised to 80-125° C. a hard and homogeneous product is obtained. If oxidation of the surface of the product is objectionable, the process may be carried out in an inert gas, e.g., nitrogen, hydrogen or carbon dioxide. Before the reaction is completed and while the product is still in soluble form it may be mixed with fillers or modifying agents, e.g., asbestos, graphite, sand, powdered metals, tar, resins, oils, colors, cellulose or acetyl cellulose and the mixtures may be subsequently hardened in molds by heating to above 100° C.

Salts of Hydroxy Acids.

Condensation by means of the neutral alkali salts of aromatic hydroxy acids, such as hydroxybenzoic and tannic, has been proposed.¹⁶ For example 100 parts of phenol, 80 parts formaldehyde and 5 to 10 parts of a 50 per cent solution of sodium potassium salicylate are mixed and heated until reaction starts. Then the heating is modified on account of the heat generated by the reaction. Upon completion of the reaction, the water contained in the initial materials is expelled by evaporation, and the mass is molded. The product of the reaction is liquid, but when the molds have cooled to about 60-80° C. they may be opened, the product being then thoroughly solidified. A period of 12 hours is sufficient for this operation.

¹⁴ J. S. C. I. 1917, 150, 1019, 1055; British Pat. 102,635, 1916; U. S. Pats. 1,235,507, 1,237,579.

¹⁵ Chem. Abs. 1917, 11, 1734; U. S. Pat. 1,216,728, Feb. 20, 1917; French Pat. 420,404, 1910.

¹⁶ Naamlouze Vennootschap, French Pat. 483,915, Aug. 21, 1917; Danish Pat. 21,606, 1916; British Pat. 117,857, 1917; U. S. Pat. 1,273,967.

Zinc and Aluminum Chloride.

The condensation of phenols with formaldehyde is accelerated by the presence of zinc chloride or aluminum chloride and the resulting product is then treated with an acid.⁷⁷ The product may be heated without becoming porous.

Ferric Chloride.

Stockhausen and Gruhl⁷⁸ knead a fluid phenolic product at 30-50° C. with salts of trivalent metals (e.g., 50 per cent ferric chloride calculated on the phenol), and with or without sulphur, rubber, filling materials, etc., and, after separation of water, they heat the mass to obtain an infusible insoluble product. In preparing an initial condensation product the reaction may be interrupted by sudden cooling, at the point of incipient turbidity. Materials, such as wood, paper, cork or fabrics, may be impregnated with the condensation product prior to its transformation into an insoluble form and then compressed and heated. The more ferric chloride added the harder the product and the shorter the period of heating required.

Sodium Sulphite.

Robinson-Bindley, Weller and Dulcken⁷⁹ condense formaldehyde, or substances yielding it, with o-, m-, or p-cresol in the presence of a neutral sulfite, e.g., sodium sulphite. The process may be carried out by vaporizing the cresol by steam, and passing the vapors with formaldehyde into a reaction chamber containing sodium sulphite at a temperature of 60-90° C.; or the cresol may be heated to 60° C. and formaldehyde gas blown through it in the presence of the catalyst. The product may be further hardened by heating at 60-100° C. and at atmospheric pressure or by heating it at higher temperatures under pressure. Scudder and Pettigrew⁸⁰ obtain a thin liquid phenolic condensation product, specially adaptable for the impregnation of friction blocks, stair treads, etc., by allowing sodium sulphite, 40 per cent formaldehyde, and carboic acid, in about the proportions of 50, 100 and 1000 parts by weight respectively, to react together for 3 or 4 days at ordinary atmospheric temperature with occasional stirring. The supernatant aqueous layer is removed, and the lower layer, containing 55-56 per cent of resin, may be used for impregnating porous articles, which are then dried at 80-90° C. and heated under pressure to harden the resin.

Sato⁸¹ treats oily condensation products with acidic or basic metallic salts under atmospheric pressure. Thus a mixture of phenol and formaldehyde in equimolecular proportions and 0.05-0.1 mol. sodium sulphite is heated at 90° C. for 2-3 hours. The oily product is freed from water and unchanged phenol and aldehyde are removed by evaporation in vacuo. Metallic salts such as copper sulphate, nickel sulphate, zinc chloride and calcium chloride and also hydrates such as those of copper or aluminum are added in proportion of 2-6 per cent, mixed thoroughly and heated at 95° C. for 5 hours and at 120° C. for a few hours. The metallic salts are added to advantage in a solution of glycerol or lactic acid. To avoid the high pressure employed in making phenol-formaldehyde condensation products and to secure a more elastic material Sato⁸² prepares a liquid product from phenol and formaldehyde with the aid of sodium sulphite and adds 5 per cent of an oxy fatty acid, e.g., glycollic, malic, lactic, tartaric or citric acids. In place of these, butyl, amyl, cetyl or myricyl alcohol likewise cholesterol, glycerol, glucose, etc. may be used.

⁷⁷ General Electric Co., J. S. C. I. 1910, 577; French Pat. 406,686, Sept. 1, 1909.

⁷⁸ J. S. C. I. 1914, 799; British Pat. 14,481, 1913; U. S. Pat. 1,150,642, Aug. 17, 1915.

⁷⁹ Chem. Abs. 1920, 807; British Pat. 134,564, Feb. 27, 1918.

⁸⁰ British Pat. 158,796, 1919; J. S. C. I. 1921, 19A; Chem. Met. Eng. 1921, 532.

⁸¹ Japanese Pat. 39,320, July 19, 1921.

⁸² Chem. Age, London, 1922, 7, 248; British Pat. 182,886, 1921.

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Sulphonated Compounds.

Tarasoff and Shestakoff¹⁴ produce solid, infusible, and insoluble products by condensing phenols with formaldehyde in presence of ammonium, alkali, or alkaline-earth salts of sulpho-acids (the so-called sulpho-aromatic fatty acids which are formed by sulphonating mixtures of fatty oils or olein with aromatic hydrocarbons) and of an acid which does not decompose such salts. For example, 300 parts by weight of cresol are gradually mixed with 135 parts of a 40 per cent solution of sodium salts of "naphtha sulpho-acids," 9 parts of hydrochloric acid (specific gravity 1.14), and 150 parts of 40 per cent aqueous formaldehyde, and heated to 65-70° C. A resinous liquid mass separates with a watery layer on top; the latter is removed and the resinous mass heated until there is a loss of 70-75 parts by weight of the total materials used. After cooling to 35-45° C. 120 parts by weight of aqueous 40 per cent formaldehyde are added and the whole mixed to a homogeneous mobile liquid, which is poured into molds, cooled, then gradually heated for one hour to 45° C., then, at intervals, by 10°-15° at a time, to 100° C.

Pollak¹⁵ uses crystallized phenol 18.8 parts, paraformaldehyde 8.73 parts and an aqueous solution of p-phenolsulfonic acid 0.04 part. The mixture is warmed on a water bath and after completion of the reaction, which ensues with a slight further rise of temperature, the product is poured into molds in which it becomes hard and insoluble at about 100° C. As an alternative method, phenol 100 parts, 40 per cent formaldehyde solution 125 parts, and hydrochloric acid (sp. gr. 1.19) 0.30 parts are evaporated and stirred on a water bath. When about 60 parts of the mixture have evaporated, reaction sets in with sufficient vigor to raise the temperature to above 100° C. and after some time a white precipitate separates from the clear solution. There is added about 30 parts of water and this is evaporated at about 75° C. The mass is then poured into molds heated to 70-80° C. and forms a solid which is elastic when warm. When the temperature is raised to 80-125° C. a hard and homogeneous product is obtained. If oxidation of the surface of the product is objectionable, the process may be carried out in an inert gas, e.g., nitrogen, hydrogen or carbon dioxide. Before the reaction is completed and while the product is still in soluble form it may be mixed with fillers or modifying agents, e.g., asbestos, graphite, sand, powdered metals, tar, resins, oils, colors, cellulose or acetyl cellulose and the mixtures may be subsequently hardened in molds by heating to above 100° C.

Salts of Hydroxy Acids.

Condensation by means of the neutral alkali salts of aromatic hydroxy acids, such as hydroxybenzoic and tannic, has been proposed.¹⁶ For example 100 parts of phenol, 80 parts formaldehyde and 5 to 10 parts of a 50 per cent solution of sodium potassium salicylate are mixed and heated until reaction starts. Then the heating is modified on account of the heat generated by the reaction. Upon completion of the reaction, the water contained in the initial materials is expelled by evaporation, and the mass is molded. The product of the reaction is liquid, but when the molds have cooled to about 60-80° C. they may be opened, the product being then thoroughly solidified. A period of 12 hours is sufficient for this operation.

¹⁴ J. S. C. I. 1917, 150, 1019, 1055; British Pat. 102,635, 1916; U. S. Pats. 1,235,507, 1,237,579.

¹⁵ Chem. Abs. 1917, 11, 1734; U. S. Pat. 1,216,728, Feb. 20, 1917; French Pat. 420,404, 1910.

¹⁶ Naamlouze Vennootschap, French Pat. 483,915, Aug. 21, 1917; Danish Pat. 21,606, 1916; British Pat. 117,857, 1917; U. S. Pat. 1,273,967.

traces of alkaline catalysts into an insoluble infusible product. This is accomplished by the addition of liquid organic acids (lactic, acetic, formic, etc.) or solid organic acids such as oxalic, tartaric, citric, gallic, or tannic acid, dissolved in a liquid organic acid. Small amounts of mineral acids also may be present. These include hydrochloric, sulphuric, phosphoric and boric acids. The conversion takes place in the cold but more rapidly on heating. The initial liquid product with the acids added can be used as a varnish, or for gluing together laminæ of wood, wood and fabric, etc. Fillers, such as pumice, sand, glass, emery, asbestos, etc., may be incorporated or the properties varied by addition of gelatin, glue, naphthalene, rubber, etc. Vessels resisting chemical reagents can be made from the final product, or laminæ or plates can be glued on surfaces by means of the initial product varnish.

Lebach⁸⁷ refers to the work of Kleberg and others in producing final condensation products by using an excess of formaldehyde and an acid as a catalytic agent. The product obtained by Kleberg presumably resembles that resulting from condensation to the ultimate stage in the presence of alkalis. Lebach found a better procedure for making hard products by acid condensation was to allow the acid catalyst to act upon a fusible soluble resin made by alkaline condensation. For instance, by adding hydrochloric acid to liquid products condensed by alkali, heat is developed and the mixture thickens and solidifies after a short time to a homogeneous block or insoluble, infusible material. While the mixture is still liquid it can be cast into molds. In this way, for example, plates for newspaper printing have been made. During the hardening, the mixture for a short time is plastic and can be kneaded into shape. Lebach has proposed the use of such a composition for dental purposes. The hardening process just described is not generally applicable for preparing electrical insulation because the insulating properties of the hardened compound usually are not sufficient.

By treating the primary product obtained by the condensation of formaldehyde and a phenol in the presence of a basic condensing agent, with sufficient acid or acid-forming substance approximately to neutralize the base, it is possible to produce "resoles," i.e., resins which form infusible masses ("resites") when heated. Using a higher proportion of acid, but insufficient to effect direct conversion into "resites" a "novolak," i.e., a resin which cannot be converted into an infusible mass by heat, is obtainable.⁸⁸

Kulas and Pauling^{88a} have proposed a two-stage process for preparing phenol-formaldehyde resin employing an acid catalyst (hydrochloric acid) in the primary reaction and an excess of base (caustic soda) in the secondary operation. The amount of base considerably exceeds that necessary to neutralize the acid and is more than 10 per cent in excess of the active phenolic body. The proportion of formaldehyde required to produce a resin by this process is said

⁸⁷ J. S. C. I. 1913, 32, 559.

⁸⁸ Bakelite-Ges. m. b. H., and R. Hessen. British Pat. 159,461, Feb. 15, 1921; J. S. C. I. 1922, 41, 771A.

^{88a} U. S. Pat. 1,414,139, Apr. 25, 1922.

to be less than for other methods. 100 parts of phenol and cresol and 50 parts of 40 per cent formalin yield 80 parts of resin. By decreasing or increasing the proportion of formaldehyde fusible or infusible resins are produced. By addition of 2-3 per cent of a hydrosulphite or a sulphite and, at the same time, about 12 per cent soap, the resin is completely soluble in benzol, or in a mixture of benzol and fatty oils.

Sulphuric Acid.

Condensation products are also obtained by Birkby⁹⁰ by reaction of phenol or its homologues with formaldehyde in the presence of dilute sulphuric acid in the proportions of 500 volumes of phenol or its homologues, 450 to 550 volumes of 40 per cent formaldehyde, and 2 to 6 per cent by volume (relatively to the phenol) of dilute sulphuric acid. The latter is prepared by mixing 20 volumes of acid of 1.84 specific gravity with 80 volumes of water. The resinification is effected at a temperature of 60 to 80° C. After reaction and removal of water, the product is neutralized by milk of lime and the remaining water is removed by heating in vacuo. The product may be finally hardened by heating under pressure.

Sulphur Dioxide.

Sarason⁹¹ conducts the condensation of formaldehyde with phenols in presence of sulphurous acid. The reaction proceeds more smoothly than when sulphuric or hydrochloric acids are used as condensing agents and the products are stated to be lighter in color and easily soluble in caustic alkalis and the majority of liquid solvents. Heinemann, Harvey and Robinson⁹² heat phenol or cresols and formaldehyde or its polymers first without a condensing agent to yield a liquid oxybenzyl alcohol, and this product is heated in an open vessel with sulphur dioxide solution. The product can be rendered insoluble by further heating or treatment with a basic catalyst. Heinemann⁹² produces condensation products from phenols, cresols, and formaldehyde by passing sulphur dioxide into the mixture of the parent materials, or a liquid hydroxybenzyl alcohol prepared therefrom, and allowing the action to proceed without the application of external heat. The process is carried out in the absence of a solvent.

Chlorine and Sodium Nitrate.

Chlorine⁹³ may also be used as a condensing agent. In this case the phenols are heated first with a portion of the required amount of formaldehyde in the presence of chlorine and then with the remainder of the formaldehyde in the presence of sodium nitrate, whereupon, after the reaction is concluded, a further heating to a temperature above 120° C. follows. For example, formaldehyde (40 per cent solution) 34 parts and crystallized phenol 46 parts are allowed to condense with 0.8 part of chlorine at 45-55° C. and when the liquid has become somewhat gelatinous, 20 parts of formaldehyde solution and 0.5 part of sodium nitrate are added. After several hours the temperature is increased gradually to 70-80° C. until a viscous transparent strongly glutinous product is obtained. The completely dried product is reddish brown. By heating to over 120° C. it becomes infusible and dissolves only in hot nitric acid.

⁹⁰ Chem. Met. Eng., 1921, 532; Chem. Abs. 15, 1060; J. S. C. I. 1921, 19A; British Pat. 153,494, 1920.

⁹¹ J. S. C. I. 1910, 410; German Pat. 219,570, March 5, 1908.

⁹² Chem. Abs. 1916, 10, 124; British Pat. 28,187, 1913.

⁹³ Chem. Abs. 1915, 9, 2801; British Pat. 9,390, 1914.

⁹⁴ Chem. Abs. 1914, 8, 2817; German Pat. 273,261, Aug. 23, 1912. Allgemeine Elektrizitäts Ges.

Carbon Dioxide.

McCoy⁹⁴ effects condensation in presence of carbon dioxide. The reaction is interrupted when the product has become infusible and insoluble but is still capable of being softened by heat and then, after shaping, the material is further heated. Conducting the process in an atmosphere of carbon dioxide serves to obviate the use of any other condensing agent. McCoy also has proposed to obtain formaldehyde by the reduction of carbon dioxide with palladium hydride and react with the formaldehyde thus obtained in the presence of carbon dioxide as a condensing agent to produce resins. The palladium hydride may be regenerated by warming in a current of hydrogen gas. The process is carried out by passing carbon dioxide into a vessel containing the hydride suspended in water. Only a part of the carbon dioxide is reduced on passage through the vehicle and the mixture of dioxide and formaldehyde is passed into a second vessel containing phenol or cresol.⁹⁵

Varying Results in Condensation.

By slight differences in the method of condensation of phenols and aldehydes, products other than resins are often produced. Stiasny conducts the condensation of phenol and formaldehyde with sulphuric acid at moderate temperatures to form water-soluble sulphonated products for tanning purposes. More vigorous heating would yield a resin. The sulphonation may also be effected after the heating of the phenol-aldehyde mixtures. In a similar way Schmidt and Andres also produce tanning materials.⁹⁶

⁹⁴ Chem. Abs. 1918, 12, 749; U. S. Pat. 1,253,261 and 1,253,262, Jan. 15, 1918.

⁹⁵ U. S. Pat. 1,253,404, Jan. 15, 1918.

⁹⁶ U. S. Pat. 1,254,364, Jan. 22, 1918.

Chapter 8.

Phenol-Formaldehyde Resins Continued. Use of Modifying Agents.

Phenol-formaldehyde resins of the fusible type possess neither toughness nor elasticity but are notably brittle. Although the infusible products are hard and strong they likewise are somewhat brittle and possess comparatively slight elasticity or flexibility. Efforts to supply these properties have been unrenmitting. If flexibility could be imparted to the product a non-inflammable material substituting for celluloid in many applications is predicted. If tough rubbery elastic qualities could be developed the application of the composition in the rubber field might follow. In the present chapter there are considered various compositions formed by adding to the phenol-formaldehyde reaction mixture or to the partially completed resin certain substances which are intended to modify the physical qualities of the product. The discussion, however, does not embrace fillers which are considered in the chapters relating to molding compositions (Chapters 24, 25 and 26). Some of the modifying agents enter into chemical combination while others are to a large extent at least merely inert additions or diluents. Proteid compounds have been given consideration in view of the numerous proposals for using glue, casein, albumen, vegetable proteids, vegetable ivory and the like. The suggestions covering proposed additions to phenol-formaldehyde resins are so numerous that space does not permit any detailed description. Modifying agents range from starch or glucose on the one hand to cholesterol and viscose on the other. The soluble phenol-formaldehyde resins of normal character dissolve only in alcohol, acetone and the like; that is, they are spirit-soluble resins and several proposals have been made with the purpose of obtaining oil-soluble resins by special methods of treatment.

Proteid Compositions.

Phenol is a powerful solvent for proteids such as glue, casein and the like and early in the history of the development of phenol-formaldehyde resins we find various suggestions for the solution of a proteid in phenol and treatment of the mixture with formaldehyde to form thermo-plastic substances. Formaldehyde, being capable of reacting with both the phenol and the glue or casein or whatever proteid was employed, was supposed to harden both of these ingredients and to

produce a product of improved elasticity. In 1907 Goldschmidt¹ employed a mixture of gelatin, β naphthol and formaldehyde for making a molding composition. He termed the formaldehyde an indurating agent as it gave to the composition a greater toughness and increased the resistance to the action of water. Also it minimized the tendency of the composition to stick to the mold. Stockhausen² incorporated gelatin with a phenol resin. Berend³ dissolved glue in phenol. For example, 150 parts by weight of glue are dissolved in 75 parts each of phenol and glycerol at 70-80° C. A mixture of 20 parts of shellac are dissolved in 40 parts of aniline. A sufficient quantity of this solution is added to 300 parts of the glue mixture to introduce 48 parts of aniline. The solutions are at 70° C. when mixed. Finally 30 parts of paraform or 80 parts of a glycerol formaldehyde mixture containing about 30 parts of formaldehyde are quickly stirred into the composition. This undergoes solidification, becoming homogeneous and tough, and is molded before it has solidified. Berend⁴ also employs casein. 25 parts by weight each of phenol and casein and 2 parts of caustic soda lye are mixed and heated until a clear viscous solution is obtained. Then 50 parts of phenol and 10 parts of trioxymethylene are added and the mixture is slowly heated to 100° C. in order to bring about reaction. Further additions of 10 parts and then 5 parts of trioxymethylene are added at intervals. The mixture is thereafter cautiously heated and is maintained at a gentle ebullition for a period of about 2 hours until a test sample shows the composition to solidify on cooling in the air. Filling materials may be added and the composition placed in molds where it is hardened by heating for 6 hours at 100-110° C. and then for a few hours at a slightly higher temperature.⁵

Sato has investigated various thermoplastic substances made from vegetable proteids, phenol and formaldehyde.⁶ The proteid is obtained from corn, beans, etc. It is incorporated with the phenolic substance and treated with formaldehyde or hexamethylenetetramine. For example, 100 parts by weight of the proteid of corn is mixed with 150 parts of phenol and the mass is kneaded, producing a thick glue-like transparent substance of light brown color. 50 parts by weight of trioxymethylene are introduced. Besides the application of these compositions in making molded articles Sato also obtains a varnish by dissolving the composition in benzol, petroleum benzine or other solvent. He claims that a lacquer can be produced which hardens at 30-40° C. to a glossy coating that is not affected by water, common organic solvents or heat up to 150° C.

¹ U. S. Pat. 1,076,417, Oct. 21, 1913.

² J. S. C. I. 1914, 605; French Pat. 466,435, 1913; German Pat. 277,653; Chem. Ztg. Rep. 1914, 573.

³ U. S. Pat. 952,724, Mar. 22, 1910.

⁴ U. S. Pat. 1,040,850, Oct. 8, 1912.

⁵ Note also Albert and Berend, J. S. C. I. 1912, 445; French Pat. 436,720, 1911.

⁶ U. S. Pats. 1,245,975, 1,245,976, 1,245,978, 1,245,979, 1,245,980, 1,245,981, 1,245,982, 1,245,983, 1,245,984, Nov. 6, 1917.

A variety of substances is employed by Tarassoff⁷ as additions to phenol-formaldehyde resins. These include albumin, casein, glue, tannin, starch, dextrine and sugar. It is claimed that the brittleness of this type of resin is reduced by the presence of such additions. Thus a mixture is made of 100 parts by weight phenol, 20 parts egg albumin, 50 parts water, 57 parts of a 37 per cent aqueous solution of sulphoacids produced from petroleum acid sludge. The mixture is heated to 80° C. until the albumin dissolves and about 50 parts of the water has evaporated. Then the mixture is cooled and 40 parts of formalin solution added. On heating to 80° C. rather violent ebullition occurs due to the reaction of condensation. The evaporation is resumed, and about 50 parts water removed, the mix cooled to 25° C. and 50 parts of formalin solution introduced. The mixture is now a rather thick liquid and is pouted into a mold and allowed to stand for 12 hours. During this time it becomes nearly solid. The molds are placed in a bath of water at 75° C. for a half hour, then heated to 90° C. for one or two hours and finally to 100° C. for the same length of time. The product is an infusible opaque yellowish solid having elastic qualities.

Kuhl⁸ heats cresol and casein with formaldehyde, with or without a small quantity of potassium carbonate, in an autoclave at 3-5 atmospheres pressure. For example, 250 grams of granular casein are soaked in 500 grams of cresol until a uniform mixture is obtained. This product is mixed with 400 grams of formaldehyde and heated in an autoclave until a pressure of 3 atmospheres is attained, and kept at this pressure for 10 minutes. The product may be dissolved in alcohol to form a varnish. According to Nakaniski⁹ casein is dissolved in a concentrated solution of borax and diluted with 10-20 parts of alcohol. Phenol and formalin are heated with sodium acetate under a reflux at about 100° C. for 2 hours and diluted with 20 parts of alcohol. By mixing the two solutions, a varnish of rich luster is made. A substitute for hard rubber proposed by Parkert is made from mica 35 parts, galalith powder 85 parts and phenol-formaldehyde resin 26 parts. The resin is put into solution in order to incorporate it with the fillers.¹⁰

Hagendorf¹¹ has used the serum from the blood of cattle, in conjunction with formic acid and trioxymethylene or formaldehyde. This mixture is heated with phenol and sodium peroxide until a solid product is obtained. Hydrogen peroxide¹² can be substituted for the sodium peroxide and other albumins may take the place of blood serum. In making knobs, buttons or other articles from proteins such as those of blood, casein or yeast, a protein powder is consolidated by the action of a colloidal solution of protein in dichlorohydrin or phenol and formaldehyde.¹³

Wiechmann¹⁴ treats vegetable ivory with phenol and reacts on the mixture with formaldehyde, obtaining a thermo-plastic substance which can be trans-

⁷U. S. Pat. 1,187,869, June 20, 1916; British Pat. 102,751, 1916; J. S. C. I. 1917, 150.

⁸J. S. C. I. 1915, 562; German Pat. 280,648, Aug. 21, 1913; Chem. Abs. 1915, 1849.

⁹Chem. Abs. 1920, 14, 2270; Japanese Pat. 34,922, Sept. 12, 1919; Cf. Japanese Pat. 31,912; Chem. Abs. 1919, 3023.

¹⁰Bottler, *Kunstharze*, 1919, 63.

¹¹J. S. C. I. 1914, 838; German Pat. 274,179, July 29, 1913.

¹²Chem. Abs. 1916, 259; British Pat. 17,728, 1914.

¹³Plauson, U. S. Pat. 1,395,729, Nov. 1, 1922.

¹⁴U. S. Pats. 1,061,346, May 13, 1913; 1,126,926, Feb. 2, 1915; 1,135,340, Apr. 13, 1915; 1,218,146, Mar. 6, 1917.

formed into a hard infusible product. The vegetable ivory in a ground condition may be mixed with a liquid or pasty form of a partial condensation product of phenol and formaldehyde. The pasty mixture is submitted to further heating until on cooling the material is hard enough to be ground. The ground material is molded. In another case ground vegetable ivory is simply mixed with a pulverized solid partial condensation product of phenol and formaldehyde. The composition is molded under heat and pressure to a hard infusible condensation product. Wiechmann is of the opinion that reaction takes place between the three essential components and that the vegetable ivory actually is in chemical combination in the molded material.

Floor Covering.

Fibrous material, before or after treatment with a phenol-formaldehyde condensation product, is disintegrated or shredded in such a manner as to preserve the original length of the fibres, and the product is kneaded to a uniform mass with rubber, casein or animal glue, together with filling material and coloring matter. The fibrous material and rubber respectively may be fireproofed by treatment with solutions of sodium silicate, zinc chloride or antimony trichloride, and also by chlorination. The composition is rolled into sheets or molded into shape, and is subsequently vulcanized.¹⁴

Oil Soluble Resins.

Phenol-formaldehyde resins normally are not soluble in fatty oils and therefore are not available for making oil varnishes without treatment to modify the solubility. The simplest method of securing an oil-soluble product is to heat the synthetic resin with a natural resin, e.g., manila or kauri copal or rosin. The latter serves as a cheap fluxing agent. Rosin esters and cumaron resin also may be used. Berend and Albert¹⁵ have investigated phenol-formaldehyde resins particularly from this standpoint. The condensation forming the phenol-formaldehyde resin may take place in the presence of the added resin, in which case the latter may exhibit some catalytic activity in accelerating condensation. An insoluble, infusible phenol formaldehyde resin may be fluxed with, for example, common rosin and the mixture put into solution in a drying oil by strongly heating. When the temperature reaches about 300° C. a reaction apparently takes place and a permanent solution of the resinous material in the oil is obtained. This may be thinned with turpentine, benzol, benzine and other solvents. Thus a fusible resin made from phenol (100 parts) and trioxymethylene (35 parts) is heated with an equal weight of rosin for ½ hour at 210-220° C. The mix then is heated for some time with linseed oil at 300° C. An infusible resin made from 100 parts cresol and 30 parts paraform, heated with its own weight of rosin to 300° C. and 5 atm. pressure is rendered soluble in fatty oils. It melts at about 150° C.¹⁶ Oil soluble products of this general character have received the name of "Albertole."

¹⁴ Frood, British Pat. 176,405, 1920; J. S. C. I. 1922, 41, 325A.

¹⁵ J. S. C. I. 1912, 886; 1913, 35; French Pat. 441,547, Feb. 16, 1912; British Pat. 1269, 1912; German Pat. 254,411, 1910; Swiss Pat. 72,631, 1916.

¹⁶ J. S. C. I. 1915, 724 and 805; 1917, 969; British Pat. 15,875, 1914; 107,205, 1916; German Pat. 281,939, 1913; U. S. Pat. to Berend, 1,191,390, July 18, 1916; 1,205,081 and 1,205,082, Nov. 14, 1916; 1,259,347, Mar. 12, 1918.

Three grades of "Albertole" described by Fonrobert¹⁷ have the following properties. One grade sinters at 130-140° C. and melts between 190-200° C. A second grade sinters at 110-120° C., melts at 150-160° C. A softer grade sinters at 90-100° C. and melts at 120-130° C. These resins are soluble in benzol, solvent naphtha, acetone, carbon tetrachloride and various petroleum distillates. They are free from ash and do not have any disagreeable odor. In order to make an oil varnish it is necessary to "run" the resin at a temperature ranging from 250-320° C. to secure a product sufficiently soluble when admixed with linseed oil to permit of addition of thinner without separation. Between 250-300° C. foaming occurs which Fonrobert considers is an indication of combination between the oil and the resin. However this may very properly be attributed to some dehydration reaction which does not involve a combination of the constituents. In making varnishes containing both linseed and tung oils it is desirable to first complete the cooking of the linseed oil before adding the tung oil.

Oil Soluble and Alkali Insoluble Resins.

Condensation products of phenols with unsaturated hydrocarbons form resins when treated with aldehydes, their polymers or compounds which hydrolyze to aldehydes; with or without the addition of neutral, acidic or basic accelerators.^{17a} Thus resins are obtained from a cresol styrene condensation product of boiling point 320-350° C. and formaldehyde. Likewise a resin is obtained from formaldehyde and a diamylene phenol condensation product of phenols having a boiling point 300-340° C. Paraform or trioxymethylene may be used in place of formaldehyde. A cresol pinene condensation product and formaldehyde and a cresol styrene condensation product and acetaldehyde also are resinous. The products are soluble in benzol and linseed oil but are insoluble in aqueous caustic alkali and alkali carbonate solutions.

Lingner¹⁸ effects the condensation of phenol by adding resin or resin acids to it and then acting on the mixture with formaldehyde in the presence of an acid (hydrochloric acid 20° B.). Vinyl compounds such as the halides, esters, amines and other vinyl compounds have been used in the condensation of phenol and formaldehyde by Plauson and Vielle.¹⁹ To accelerate the reaction they use an organic anhydride. The products are fusible and suitable for varnishes and molding purposes.²⁰

Tung Oil.

Brown²¹ found that if a drying oil and a drier are mixed with cresol and formaldehyde, and the mixture heated, the materials yield a varnish composition. He makes use of cresol, formaldehyde, tung oil and as a drier a mixture of lead-manganese tungate and lead-manganese resinate. An example follows. Twelve parts of raw Chinese wood oil and 1.5

¹⁷ *Kunststoffe* 1922, 12, 121.

^{17a} Bakelite Ges. m. b. H., German Pat. 340,989, May 4, 1919; J. S. C. I. 1922, 41, 23A.

¹⁸ French Pat. 386,002, Jan. 15, 1908; Chem. Abs. 1909, 3, 2360.

¹⁹ British Pat. 156,151, 1920; Chem. Abs. 1921, 1821.

²⁰ See Chapter 18.

²¹ U. S. Pat. 1,212,738, Jan. 16, 1917.

parts of drier are heated in an open kettle to 180-190° C. as rapidly as possible and maintained at that temperature for about fifteen minutes. The liquid is then allowed to cool to 100° C. Four parts of cresol are added and stirred in well with the oil, and finally three parts of formalin are added. The temperature of the mixture is maintained at 95-100° C. for one hour, and the liquid is stirred at frequent intervals. After one hour, most of the water should be evaporated, which will be indicated by a rise in temperature above 100° C. At this point, the heating should be stopped and the mixture be permitted to stand for several hours. The procedure results in a liquid which separates into a layer of clear varnish and a layer of precipitated sediment, the latter containing most of the tungate-resinate drier. The tung oil has absorbed a portion of the drier, and the remainder, which has reacted with the formaldehyde present to form a precipitate, is of no value. The clear liquid is decanted from the precipitated sediment, and heated slowly to 150° C. The varnish does not dry hard in the air without the application of heat.

Cumaron Resin and Tung Oil.

McCoy²² incorporates cumaron or indene resins or polymerized tung oil with phenol-formaldehyde resins in order to retard hardening and facilitate molding. Compositions with these ingredients are suitable for use by either the hot or cold process of molding.

Castor Oil.

A flexible condensation product has been produced by Robinson²³ which can be bent, or molded by heating it to about 120° C. It is produced by heating cresol 750 parts, formaldehyde (40 per cent) 675 parts, ammonia (sp. gr. 0.880) 90 parts, and castor oil 50 to 80 parts. The oil may be added at first, or after partial condensation has taken place and the aqueous layer that separates has been removed. The final hardening is carried out in the usual manner by heating in an inert atmosphere. The castor oil may be replaced by camphor, linseed, rape, cottonseed or other oils.

Stearine Pitch.

Barringer²⁴ mixes phenol formaldehyde resins with stearine pitch from cottonseed oil refining and amyl acetate as a solvent. The mixture is applied to a fibrous carrier such as cambric. Insulation produced in this manner remains flexible indefinitely and its resistance increases with rise in temperature up to 73° C.

Japanese Lac.

Phenol or cresol have been condensed with formaldehyde in the presence of Japanese lac.²⁵ The product is soluble in essential or fatty oils and its use has been recommended in paints. A method of preparation is to mix 100 parts of phenol or cresol, 200 parts of formalin (35 per cent) and 50 parts of Japanese lac. The mixture is heated to 120° C. for several hours.

²² U. S. Pat. 1,425,784, Aug. 15, 1922.

²³ British Pat. 136,298, 1918; J. S. C. I. 1920, 164A; Chem. Abs. 1920, 1196.

²⁴ U. S. Pat. 1,091,621, Mar. 31, 1914; Chem. Abs. 1914, 8, 1877.

²⁵ Hatta, Nakajima and Kaisha, Jap. Pat. 39,310, July 18, 1921; Chem. Abs. 1922, 16, 2787.

Oxidized Oils.

Caroselli²⁰ prepares rubbery products by treating mixtures of oxidized oils and phenols with formaldehyde, in the presence of a condensing agent. Hydrochloric and sulphuric acids are the only condensing agents mentioned. Vegetable and animal proteids, such as albumin, casein, blood, and milk, or sugars may be added. In one example, 4 kilos naphthol are dissolved in 50 kilos oxidized castor oil, and treated with a mixture of 20 kilos 30 per cent formalin and 2½ kilos hydrochloric acid. When heated to 90-100° C. an elastic solid is said to be formed.

Saponified Oils.

Wennagel²¹ saponifies a phenol solution of about equal parts of vegetable or animal oils and resin (colophony) with a large excess of caustic alkali and then treats the mixture with formaldehyde to obtain odorless, transparent, hard and elastic products. Wennagel also separately prepares the soaps and resinsates and heats with a phenolic body. Formaldehyde is added and the heating continued for a time. The product is dried and finally baked at a gradually rising temperature. Reeser²² similarly to Wennagel, mixes fats and oils with the condensation products and then saponifies the mixture. Chappell²³ uses oleic acid with phenol formaldehyde resins.

Sulphonated Oils.

Tarasoff²⁴ obtains condensation products by the action of aldehydes, such as formaldehyde upon mixtures of phenols with sulphonated fats and oils, as, for instance, sulphonated castor-oil, prepared by treating 100 parts by weight of oil with 30 parts of sulphuric acid (specific gravity 1.842), and washing the product with water and a solution of common salt. For example, 200 parts of commercial carbolic acid are mixed with 50 parts of sulphonated castor oil, 130 parts of 40 per cent formalin, and 200 parts of water acidified with sulphuric acid. The mixture is stirred and heated until the reaction begins. The resinous mass obtained is washed with water and with a solution of sulphur dioxide in order to keep it colorless. About 300 parts of a white, opaque, fusible product are obtained. He has also used sulphonated resin oils in preparing moldable products.²⁵

Factis.

Fatty oils which have been treated with sulphur chloride to make "oil rubber" or "factis" are considered by McCoy^{31a} to be a desirable addition to phenol-formaldehyde condensation products. See Chapter 19.

Turpentine.

Tarasoff and Shestakoff²² harden phenolic condensation products by mixing them with oil of turpentine or other liquid terpene products, or with coal or wood tar, or non-phenolic oils obtained in the distillation of coal tar. The

²⁰ U. S. Pat. 1,086,139, Feb. 3, 1914.

²¹ U. S. Pats. 1,107,003, Aug. 11, 1914; 1,197,316, Sept. 5, 1916; J. S. C. I. 1915, 1071.

²² J. S. C. I. 1916, 1164; French Pat. 479,319, 1915.

²³ U. S. Pat. 1,102,473, July 7, 1914.

²⁴ J. S. C. I. 1914, 557; 1915, 187; 1916, 983; British Pats. 528; 6716; 7560, 1914; French Pats. 469,832; 470,810, 1914; U. S. Pats. 1,216,515; 1,216,516, Feb. 1917; 1,187,869.

²⁵ U. S. Pat. 1,235,507, July 31, 1917.

^{31a} U. S. Pat. 1,194,201, Aug. 8, 1916.

³¹ J. S. C. I. 1917, 559; British Pat. 104,887, 1916; U. S. Pat. 1,252,507, Jan. 8, 1918.

initial stage of the process is carried out at a temperature below the boiling point of the mixture, and in the presence of fixed alkalis, ammonia, or organic bases. The resulting product has good dielectric properties and is not affected by various chemical agents. Van Voorhout³⁵ drives off the water from the phenolic product by heating and adds turpentine and glycerol to prevent too great rise in temperature.

Rubber Compositions.

A hard rubber composition prepared by Baekeland³⁴ is produced by mixing with rubber a brittle phenol-formaldehyde resin in powdered form representing an intermediate stage of condensation. Catalysts may be present to bring about the formation of an infusible resinous product on vulcanization of the rubber. Aylsworth,³⁶ on the other hand, completely hardened a phenol-formaldehyde resinous condensation product to an infusible and insoluble condition before incorporation with rubber, and in the powdered form exposed the resin to a temperature of about 260° C. (500° F.) to remove any free phenol, moisture or ammonia. The hardened condensation product was used in proportions varying between 30 and 90 per cent of the total composition. Vulcanization was carried out at the usual vulcanizing temperature. Another procedure, recommended by Aylsworth,³⁶ was the treatment of a hard and completely reacted porous sponge of a condensation product of phenol and formaldehyde by boiling for several hours with a 10 per cent solution of caustic soda or potash. The residue was washed and 2 to 4 parts mixed with 3 to 1 parts of rubber. Sulphur was added and the composition was vulcanized by heating. The molded and vulcanized material when used for battery jars containing a strong alkaline electrolyte was treated with caustic alkali to remove any excess of the vulcanizing agent. Benjamin³⁷ mixes rubber stock and a vulcanizing agent with asbestos, mica or other mineral filler, the particles of which are coated with a primary soluble resinous condensation product of phenol and formaldehyde. The mixture is hardened by heating. A resilient gasket or packing material can be made from this composition. The completed material contains less than one per cent of uncombined sulphur. A phenol-aldehyde resin, which is fusible and soluble, forms an ingredient of a rubber mixture,^{37a} the subsequent treatment being such that the condensation product is not rendered non-plastic. Commercial carbolic acid is mixed with an equal volume 40 per cent formalin and 5 per cent ammonia solution. This is heated until reaction commences and the temperature is maintained at about 80° C. until a plastic mass results. 20 per cent of this mass is mixed with 40 per cent rubber, 7-8 per cent sulphur and the usual fillers, and the composition is vulcanized for 2 hours at 138° C.

³⁴ Chem. Abs. 1918, 983; French Pat. 423,417, 1917.

³⁵ U. S. Pat. 1,200,692, Oct. 10, 1916.

³⁶ U. S. Pat. 1,111,284, Sept. 22, 1914.

³⁷ U. S. Pat. 1,092,511, Apr. 7, 1914.

^{37a} U. S. Pats. 1,409,275, 1,409,276 and 1,409,277, March 14, 1922.

³⁸ Speedy and Crouch, British Pat. 171,803, Aug. 31, 1920.

Rubber and Vegetable Ivory.

A mixture of rubber, vegetable ivory and phenol-formaldehyde resin in equal proportions is employed by Wiechmann³⁸ as a plastic composition. Rubber or rubber substitute, vegetable albumin and phenol-formaldehyde resin may be incorporated on mixing rolls.³⁹

Melamid⁴⁰ obtains resin-like substances by condensing a phenol and formaldehyde to produce a phenol-alcohol, which is subsequently esterified in caustic soda solution with a benzol solution of an aromatic sulphochloride. For example, 100 kg. of cresol-alcohol produced from commercial cresol mixture and formaldehyde are dissolved in 300 kg. of 10 per cent caustic soda solution and stirred for several hours at a temperature not exceeding 30° C. with a solution of 137 kg. of a mixture of o- and p-toluene sulphochloride or one or other of these isomers in 500 kg. benzol. The benzol is washed free from alkali, dried, and the residual resin obtained by evaporation. The initial phenol-alcohol may be produced in the presence of the aromatic sulphochloride and the product further treated with sulphochloride. Phosgene or an organic acid anhydride, e.g., acetic anhydride, may be employed in place of the sulphochlorides.

Non-Darkening Phenol-Formaldehyde Resins.

Melamid's observations, according to Jacobsohn⁴¹ have resulted in the development of a light-yellow odorless resin of notable stability of color in the presence of light and air. A soluble resin of low melting point first is prepared from cresol and formalin, using a small proportion of hydrochloric acid as a catalyst. This resin is esterified with para toluene sulphochloride.⁴² The resin also may be acetylated. Protection of the hydroxyl groups resulting from this treatment lends color stability to the resin. Phenols treated with sodium bisulphate and thiosulphate are claimed by Pfautsch⁴³ to be capable of conversion into artificial resins which do not discolor on keeping.

Bucherer⁴⁴ likewise recommends that the free phenolic groups of the resinous condensation products from phenols and formaldehyde be substituted by organic radicals, such as alkyl, aralkyl, or acyl groups, to render the products insoluble in alkali, and to modify their solubility in organic solvents. Para-toluene sulphonic, benzoic, salicylic, cinnamic, acetic, valeric and brom-valeric esters, benzyl ethers and the mixed ether-esters are soluble in various organic solvents; the carbonic esters are practically insoluble and of high melting point; they may be prepared *in situ* upon textiles, wood, paper, etc., by treating with carbonyl chloride the material impregnated with alkaline solutions of the resins.

Knoll und Co.⁴⁵ report that the dark color of their earlier products (see Chap. 6) can be reduced by a further addition of aldehyde beyond that stated. For example, 110 parts of phenol, 100 parts of 40 per cent formaldehyde and 5 parts of sodium carbonate are heated until all the carbon dioxide is given off; 50 to 60 parts of water are then distilled off *in vacuo* from the product, and the resin obtained is mixed with 75 parts of potato starch. The mass is cooled and 100 parts of a mixture of 1 part of fuming hydrochloric acid and 4 parts of 40 per cent formaldehyde added, after which it is placed in molds and

³⁸ U. S. Pat. 1,067,855, July 22, 1913.

³⁹ Wiechmann, U. S. Pat. 1,067,856, July 22, 1913.

⁴⁰ British Pat. 137,291, 137,292 and 137,293, Dec. 29, 1919; J. S. C. I. July 30, 1921, 520A; Chem. Abs. 1920, 852, 1450, 1451, 2865.

⁴¹ Kunststoffe, 1921, 11, 105.

⁴² A by-product of saccharin manufacture.

⁴³ Kunststoffe, 1922, 12, 109; J. S. C. I. 1922, 41, 93A; German Pat. 341,231, 1919.

⁴⁴ Chem. Abs. 1921, 15, 183, 319; British Pats. 148,139 and 148,366, 1920.

⁴⁵ French Pat. 397,051, Dec. 3, 1908, J. S. C. I. 1908, 908; 1909, 803, 843; 1911, 1125; 1912, 399; British Pat. 27,096, 1908; 6430, 1911.

heated for about 15 minutes at 60° to 80° C. The product is washed with dilute sodium carbonate solution.

In the manufacture of colorless⁴⁶ or very light-colored insoluble condensation products from phenols and aldehydes, the color-forming constituents of the readily condensable intermediate products are removed by extraction agents such as ether.

Phenyl Derivatives.

The incorporation with various phenyl derivatives such as anisol, phenyl methyl ketone or methyl benzoate in conjunction with hexamethylene tetramine or hydrobenzamide has been proposed. The substances should be used in the approximate ratio of one phenyl group in the phenol and in the phenyl derivative to one methylene group in the hexa or hydrobenzamide. During the reaction ammonia is evolved, and the mixture gradually becomes viscous and solidifies on cooling. At this stage the compound is soluble in alcohol and some other solvents, and may be used as a varnish, etc. The reaction may be carried on up to this stage by boiling a solution of the mixture in alcohol or other non-aqueous solvent. Further heating of the compound produces an infusible, insoluble substance, which may be used as a substitute for amber, as an electrical insulator, etc. The liquid mixture, after short treatment, may be used as a binder for substances like carborundum.⁴⁷

The phenyl esters of inorganic oxy-acids are recommended by Baekeland⁴⁸ as plasticizing agents. Ortho-cresyl-phosphate or a mixture of cresyl phosphates containing a major proportion of the ortho compound may be used. The corresponding silicates, titanates, borates and molybdates also may be employed. As a rule from 20 to 60 parts by weight of phenyl ester is employed for 100 parts of the phenol formaldehyde resin.

By incorporating a di-azo compound with a synthetic resin before completing the condensation colored resins and oil soluble dyestuffs are derived by Plauson and Vielle.⁴⁹ The resins used are those obtained by condensation or polymerization of phenols and aldehydes, or ketones and aldehydes. The products may be used as fat or oil-soluble varnishes for paper, textile fabrics, leather, wood or metals, or as an electrical insulator.

Favolle⁵⁰ obtained by the following procedure a product claimed to be serviceable in rendering fabrics waterproof and as an electrical insulator. 2 parts by weight of sulphuric acid (66° B.) are added to 1 part of glycerol, the mixture is allowed to cool, and from 1 to 1½ parts of formalin (40 per cent) are then added. The mixture is again cooled, and, after adding 5 parts of water, 1¼ parts of phenol are slowly poured into it with constant stirring and external cooling. The mixture is then left at rest for 20 hours, when the product will be found as a layer on the surface of the liquid. Gradual hardening occurs on exposure to the air. The formaldehyde may be replaced by methylal and the phenol by cresol. Another formula is glycerol 1 part, strong sulphuric acid 2.2-3.3 parts, 40 per cent formaldehyde 1 part, water 0.7-1 part, phenol 2-3 parts. When the amount of phenol is limited to one part, the product is obtained by vigorous stirring with 10-20 per cent by weight of concentrated sulphuric acid; if more phenol is used it may be necessary to heat on the water bath, and incorporate 10-20 per cent of flowers of sulphur, or further to add casein, starch, or other carbohydrate. When only 0.7 part of phenol is employed,

⁴⁶ Chem. Abs. 1911, 5, 2745; German Pat. 233,395, Feb. 27, 1910.

⁴⁷ Wade, Karpen, J. S. C. I. 1915, 623; British Pat. 9292, 1914. Redman, U. S. Pat. 1,209,333, Dec. 19, 1916.

⁴⁸ U. S. Pat. 1,439,056, Dec. 19, 1922.

⁴⁹ Chem. Age, London, 1922, 7, 212; British Pat. 182,497, 1921.

⁵⁰ J. S. C. I. 1904, 195 and 448; French Pat. 335,584, Sept. 26, 1903; the addition to an initial phenol aldehyde resin of glycerol acidulated with hydrochloric acid is proposed by Drummond. British Pat. 184,961, 1921; Chem. Abs. 1923, 188. Hypophosphorus acid is recommended as a bleaching agent.

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³⁸ U. S. Pat. 1,067,855, July 22, 1913.

³⁹ Wiechmann, U. S. Pat. 1,067,856, July 22, 1913.

⁴⁰ British Pat. 137,291, 137,292 and 137,293, Dec. 29, 1919; J. S. C. I. July 30, 1921, 520A; Chem. Abs. 1920, 852, 1450, 1451, 2865.

⁴¹ Kunststoffe, 1921, 11, 105.

⁴² A by-product of saccharin manufacture.

⁴³ Kunststoffe, 1922, 12, 109; J. S. C. I. 1922, 41, 93A; German Pat. 341,231, 1919.

⁴⁴ Chem. Abs. 1921, 15, 183, 319; British Pats. 148,139 and 148,366, 1920.

⁴⁵ French Pat. 397,051, Dec. 3, 1908, J. S. C. I. 1908, 908; 1909, 803, 843; 1911, 1125; 1912, 399; British Pat. 27,096, 1908; 6430, 1911.

25 parts of a phenol ester added. 212 parts of 40 per cent formalin and about 5 parts concentrated ammonia are introduced and the mixture boiled several hours. The water which separates is decanted and the mass further heated. The product may be used as a coating. Fillers may be added. Weller and Robinson-Bindley⁵⁶ effect condensation in the presence of a very small proportion of nitrocellulose or cellulose acetate; the maximum amount of cellulose ester used is about 0.8 per cent figured on the phenol. In an example, cresylic acid, formaldehyde, sodium hydroxide, and cellulose acetate are employed. The liquid product is boiled down, baked at atmospheric pressure, and may be further treated in an autoclave. Camphene and nitrocellulose are added to a phenol-formaldehyde condensation product using acetone as a solvent.⁵⁷ This product is proposed as a substitute for celluloid.

Viscose.

Collardon⁵⁸ mixes condensation products of phenols and aldehydes, while in paste-like form, with cellulose xanthate or sulphohydrocellulose or both, and the mass is steamed and washed to remove alkali and sulphur compounds. Or the cellulose xanthate may be steamed and washed prior to its incorporation with the condensation product. A small amount of resinous rubber or resins or both may also be introduced. Products for electrical insulation are made by mixing cellulose xanthate, or sulphohydrocellulose with a small proportion of resinous rubber so as to make the composition waterproof and fairly flexible. The mixture is then steamed and washed. An addition of sulphur, zinc sulphide, or filling materials may be made. By Taylor's method⁵⁹ alkali-cellulose is treated with 50 per cent of carbon disulphide in a closed vessel and the mixture is allowed to stand for eight hours at room temperature, then enough water is added to form a covering. A phenol-formaldehyde mixture is now added in varying proportions and reacted to form a solid product which can be hardened by heat and pressure. Collardon⁶⁰ mixes a phenol-formaldehyde condensation product with viscose, by working together on differential rolls. The product is steamed, washed and then heated to 130-150° C. Viscose silk threads up to 1 denier in fineness are produced by spinning raw viscose with phenol-aldehyde condensation products in a bisulphite bath, the concentration of the bath being inversely proportional to the thread fineness to be produced.⁶¹

⁵⁶ British Pat. 152,384, 1919; Chem. Abs. 1921, 1060; J. S. C. I. 1920, 792A; Chem. Met. Eng. 1921, 271; U. S. Pat. 1,368,867, Feb. 15, 1921; Chem. Abs. 1921, 271, 1381.

⁵⁷ Chem. Abs. 1920, 1196; U. S. Pat. 1,331,127; Chem. Abs. 1920, 808; British Pat. 134,565, 1918.

⁵⁸ J. S. C. I. 1913, 498; British Pats. 1598 and 1599, Jan. 20, 1912; Chem. Abs. 1916, 2418; Swedish Pat. 40,613, 1916.

⁵⁹ U. S. Pat. 1,172,073, Feb. 15, 1916.

⁶⁰ Austrian Pat. 82,803; Kunststoffe 1921, 159.

⁶¹ Bronnert, U. S. Pat. 1,374,718, Apr. 12, 1921; Chem. Abs., 1921, 15, 2730.

Softening Agents.

In preparing insulating varnishes for electric coils, etc., Baekeland⁶² uses solvents boiling above 120° C., such as naphthalene, xylene, nitro-benzene, and other hydrocarbons or their homologues or mixtures of these, to reduce the shrinkage of the resin and soften it at high temperatures. He also employs permanently fusible resins, e.g., those from phenol and formaldehyde. The use of small quantities of these softening agents eliminates the brittleness and inflexibility which is an inherent property of hardened phenol-formaldehyde resins. Likewise Baekeland forms particles or fragments of an infusible composition containing a phenolic condensation product in solid solution with naphthalene, anthracene or other solvent of high boiling point. After transformation into the final state, the particles or fragments are capable of being welded together into coherent masses under the action of heat and pressure. These products are plastic.⁶³ Aylsworth^{63a} also has made similar products containing a relatively non-volatile chlornaphthalene or nitronaphthalene derivative, which dissolves in and renders plastic the product at about 175° C. The product is free from any halogen acid and is insoluble in alcohol and water. Acetanilide, ricinoleic acid, and dinitrobenzene may also be used. A resin is made by Mannesmann⁶⁴ from phenols, especially m-cresol, and aldehydes in presence of chlorinated hydrocarbons, but without acid or alkaline catalysts. Monochlornaphthalene is especially appropriate as a solvent ingredient for compositions which are to be hardened by subsequent heating, because it is liquid at room temperatures, but remains in the hardened composition, apparently in the condition of solid solution as a desirable plasticizing ingredient. Cresol formaldehyde resin is soluble in monochlornaphthalene in all proportions and the latter is similarly soluble in cresol resin in all proportions by the aid of heat. Phenol formaldehyde resin and monochlornaphthalene, however, are not mutually soluble in all proportions. Monochlornaphthalene is soluble in phenol resin when heated therewith in proportions of approximately equal parts. Larger amounts of monochlornaphthalene do not remain in solution with the phenol resin. Enamel or lacquer compositions which are to be hardened by subsequent heat treatment may be made by compounding cresol-resin and hexamethylenetetramine, with free cresol and a fluid chlornaphthalene. The proportions of the latter ingredient may vary in wide limits, for example, the monochlor compound up to twice the weight of the cresol resin; depending on the desired fluidity and character of the varnish or lacquer desired. Free cresol also may be added in wide limits and if used in large percentages, the amount of hexa is proportionally increased.

Free cresol is used, if monochlornaphthalene is the solvent, for the purpose of thinning the composition and also because a better impreg-

⁶² U. S. Pat. 1,156,452, Oct. 12, 1915.

⁶³ U. S. Pats. 1,259,472 and 1,259,473, Mar. 19, 1918.

^{63a} J. S. C. I. 1914, 1063; U. S. Pat. 1,111,285, Sept. 22, 1914.

⁶⁴ Chem. Abs. 1920, 1227; Dan. Pat. 24,697, June 30, 1919.

nating varnish, for coils and the like, is made. In such a composition, the hardening agent, hexamethylenetetramine, or tri-oxy-methylene or some other solid anhydrous polymer of formaldehyde, is supplied in the proportion of 3 or 4 per cent of the weight of the cresol resin and an additional amount in the proportion of 20 to 25 per cent of the weight of the free cresol used. Also, in some cases, solid chlornaphthalenes or chlorphenols may be added to the solution since they have the property of reducing the shrinkage of the varnish film during and after hardening; the coefficient of expansion of the cresolic compositions being greater than that of resins made from phenol.⁶⁵

Chlorphenols.

A resin which is practically non-inflammable and highly resistant to chemical reagents is prepared by Steinmetz⁶⁶ by mixing a halogenated phenol with formalin and heating with a catalyzer under a reflux condenser. This product is fusible but is hardened by addition of hexamethylenetetramine. Aylsworth uses halogen derivatives of phenol or cresol such as pentachlorophenol as solvents or plasticizing agents. These chlorinated compounds are useful in molding operations to render the composition more readily flowable. When the composition contains hexamethylenetetramine, the ammonia, which is liberated during the reaction, due to the hardening of the resin, is absorbed, in part at least, by the chlorinated compound.⁶⁷

Anhydro-Formaldehyde-Aniline.

Baekeland⁶⁸ used aniline as a solvent or flux for infusible phenol-formaldehyde resins. Aniline has a pronounced softening action on these resins, especially at high temperatures, and permits infusible particles or fragments to be welded together into compact coherent masses under heat and pressure. Later⁶⁹ Baekeland employed anhydro-formaldehyde-aniline. This substance, in contradistinction to hexamethylenetetramine, liberates no gaseous or readily volatile by-product in the hardening of the resin from fusible to infusible state. The addition of anhydro-formaldehyde-aniline up to 110-130 parts to 100 parts of fusible resin is accompanied by increasing hardness of the final product, while still higher proportions show increased plasticity at high temperatures. The fusible resin and anhydro-formaldehyde-aniline are incorporated with a hydrocarbon solvent, such as "neutral oil." He

⁶⁵ Note Aylsworth, U. S. Pat. 1,087,422, Feb. 17, 1914; Reissue 14,530 and 14,531, Oct. 18, 1918. Redman, Weith and Brock, U. S. Pat. 1,242,593, Oct. 9, 1917, also use naphthalene, anthracene, creosote oils, camphor, etc., as plasticizing agents.

⁶⁶ U. S. Pat. 1,215,072, Feb. 6, 1917; J. S. C. I. 1917, 396.

⁶⁷ J. S. C. I. 1911, 1267; 1912, 546; 1913, 35, 298; 1914, 931; U. S. Pats. 1,046,137, Reissued 13,531, Feb. 11, 1913; 1,046,420; 1,102,634; Brit. Pat. 9559, 1911; French Pat. 429,292, May 5, 1911.

⁶⁸ U. S. Pat. 1,133,083, Mar. 23, 1915.

⁶⁹ U. S. Pat. 1,216,265, Feb. 20, 1917.

also⁷⁰ used a chlorinated hydrocarbon with anhydro-formaldehyde-aniline. Symmetrical dichlorethane, tetrachlorethane and monochlor-naphthalene are specified.⁷¹ Goldsmith^{71a} obtains a compound which is soluble in acetone and has the physical characters of a resin by heating together a phenol or a fusible phenol resin and anhydro-formaldehyde-aniline.

Sulphite Waste Liquor.

An interesting method of making resins is that proposed by Knight.⁷² The waste liquor is concentrated, fermented and according to one procedure the alcohol is removed. The concentrated liquor is treated with phenol or cresol at atmospheric pressure or at higher pressures in the presence of an acid or alkaline condensing agent. Hydrochloric acid, zinc chloride, caustic soda, sodium thiosulphate, calcium hydroxide and ammonium carbonate are mentioned. From 2 to 10 per cent of catalyst is used based on the weight of phenol employed. The latter is roughly equal to the weight of the total solids in the liquor. When the mixture is heated above the boiling point of water for about an hour separation occurs into two layers, one of aqueous composition and the other containing the condensation product. This product upon further heating either with or without special condensing agents yields solid substances generally of a resinous nature. The products are proposed as substitutes for shellac, in making varnishes or as rubber substitutes. On further heating insoluble bodies adapted for insulating purposes are obtained. By another procedure the alcohol produced by fermentation is allowed to remain in the liquor and is oxidized to aldehyde. On treatment of the oxidized liquor with phenol, condensation products with both the lignone compound and the aldehyde are obtained.

Acetaldehyde from Sulphite Waste Liquor.

By fermenting concentrated sulphite waste liquor and treating with an oxidizing agent such as sodium dichromate Knight⁷³ obtains acetaldehyde. The mixture is treated with phenol in the presence of a catalyst. A resin is obtained composed of the phenolic condensation products of acetaldehyde and lignone. In one case a waste liquor which had been fermented and contained 100 parts total solids and about 1 part of alcohol was treated with 8 parts of potassium dichromate and 101 parts of phenol yielding 140 parts of a solid condensation product by heating under pressure to 120° C. Iron salts, e.g., ferric chloride and sulphate, may be used as catalysts. Also prior to the step of condensation various nitro, chlor or amido compounds may be added.

Acetaldehyde and Phenol.

A condensation product from acetaldehyde and phenol or cresol is employed by Novotny⁷⁴ for impregnating fibrous blanks which are to be used for making

⁷⁰ U. S. Pat. 1,216,266, Feb. 20, 1917.

⁷¹ See also Baekeland and Gotthelf, U. S. Pat. 1,217,115, Feb. 20, 1917; J. S. C. I. 1917, 453.

^{71a} J. S. C. I. 1916, 317; 1917, 894; U. S. Pat. 1,228,428, June 5, 1917; see also U. S. Pat. 1,168,626; 1,188,239; 1,230,829.

⁷² U. S. Pat. 1,143,714, June 22, 1915.

⁷³ U. S. Pat. 1,143,714, June 22, 1915.

⁷⁴ U. S. Pat. 1,370,666, Mar. 8, 1921.

phonograph records, printing plates, panels, gears, etc. One hundred parts of phenol and 75 parts of acetaldehyde are brought into reaction by means of a catalyst;—hydrochloric or sulphuric acid. The acid is removed by blowing with steam or by neutralizing with ammonia. The product does not harden readily on heating but retains its thermoplastic properties and may be readily cold-molded. Protracted baking in an oven will bring about hardening to an infusible form. The addition of 2 per cent of nigrosine black or zinc chloride as a final catalyst assists in the hardening. An intermediate product may be made from 100 parts of phenol to 35 parts of acetaldehyde, reacting in the presence of an acid and adding the acetaldehyde compound with sodium bisulphite as a hardening agent. Impregnation of paper, cardboard or other support is effected by using a solution of the condensation product in a mixture of benzol and alcohol. One part of the condensation product to 20 parts of solvent is recommended by Novotny.

A resin prepared in the author's laboratory from para acetaldehyde and phenol proved to be applicable in a series of molding compositions tested experimentally. A hard brittle resin was obtained by slowly adding paraldehyde in the proportion of 4 lbs. to phenol 8 lbs. containing 1 fl. oz. of concentrated hydrochloric acid. The mixture became hot and was allowed to stand over night. Then it was heated to 150° C. under reflux for 1 hour. This resin, with 10 per cent of hexa, dissolved in an equal weight of denatured alcohol was incorporated with a weight of wood flour equal to the weight of the resin. The mix was dried in a vacuum drier. In the press thin test discs were molded and these cured readily in 2 minutes at 160° C. (320° F.) and 1000 lbs. pressure. The surface of the molded pieces was satisfactory and the color was light brown.

A phenolic condensation product, permanently fusible below 218° C., is obtained by heating together in a closed digester at 200°-220° F. (93°-104° C.), a phenol and acetaldehyde or a polymer in the presence of a quantity of an inorganic acid condensing agent, e.g., hydrochloric or sulphuric acid, not exceeding 0.5 per cent of the phenol used, until the acetaldehyde has substantially all reacted with the phenol. During the reaction external heating is stopped and a cooling medium applied to the digester to maintain the temperature within the specified limits. Excess of phenol and water are removed from the product, by distillation, and the acid condensing agent is also removed, or neutralized and separated. The fusible resin thus obtained may be treated with hexamethylenetetramine, so as to form an infusible substance on the application of heat.⁷⁶

Miscellaneous Procedures.

Amber-like substances such as are used in pipe stems and for other purposes, made from resorcinol heated with formaldehyde, have been produced by Peter.⁷⁶

⁷⁵ Kendall, British Pat. 159,164, Nov. 17, 1920; J. S. C. I. 41, 558A.

⁷⁶ J. S. C. I. 1915, 914; U. S. Pat. 1,147,264. Farugi and Cioni, Boll. Chim. Farm. 1919, 58, 101; J. S. C. I. 1919, 427A, have described the irritation of the mucous membrane caused by the use of some imitation amber mouth-pieces. This they attribute to the freeing of formaldehyde from a casein compound by action of smoke and saliva. Sachs, Wiener klin. Wochschr., 1921, 34, 356, states that the manufacture of artificial amber (bakelite is specified) in Austria has led to increasing numbers of cases of dermatitis directly due to exposure to the fumes of phenol, formaldehyde and ammonia in the plants. He describes suitable therapeutic measures and urges proper protection for the workers. Cases of dermatitis are known which are attributed to the use of phenol-formaldehyde resin varnishes by hyper-sensitive persons, but these are of comparatively rare occurrence. As noted in Chapter I a varnish resin made by synthetic means may be expected to have its detractors among those bound by the traditions of natural resin products. A phenol-formaldehyde resin varnish

A resinous substance which remains soluble and fusible on heating is produced by condensing phenol or its homologues with acetaldehyde or its polymers. Formaldehyde or its polymers may be added, if desired, at any stage of the process in order to reduce the solubility and fusibility of the resulting product.^{76a} Labbe⁷⁷ has treated catechol, resorcinol, quinol, pyrogallol, etc., with a cold 40 per cent solution of formaldehyde in presence of an acid to form a mass which soon becomes gelatinous, and after some hours is converted into a homogeneous, elastic substance. Hard products are obtained by diluting the formaldehyde solution with half its volume of water. These products are insoluble in water and organic solvents, unattacked by acids and alkalis, and are non-inflammable. The addition of acetone or glycerol to the formaldehyde results in the production of transparent masses. The physical properties of the products may be further modified by incorporating carbohydrates or cellulose. McCoy⁷⁸ uses pyrogallol and paraform in presence of gum arabic to produce a red infusible resin. Andresen⁷⁹ condenses eugenol with formaldehyde and obtains a resin suitable for dental use. The reacting materials may be mixed with burnt alum, and the pasty condensation product mixed with zinc oxide.

Acrolein has been used by Moureu to form hard resins with phenols. Condensation is carried out in the presence of traces of inorganic or organic bases. Instead of acrolein, its polymerization products, described in Chapter 10, may be employed. The resins are non-conductors of electricity and may be used for molding purposes and impregnation of insulating material.⁸⁰

From aromatic hydroxycarboxylic acids and aldehydes a series of resins soluble in mild alkalis has been obtained by Meister, Lucius, and Brünig.⁸¹ The acid is heated with the aldehyde, with or without the presence of acid or basic condensing agents. For example, salicylic acid may be heated with 30 per cent formaldehyde and water for 20 hrs. and the whitish precipitate produced separated, freed from excess of water and further heated until a sample sets to a clear glass-like substance. The duration of treatment may be shortened by adding a catalyst such as hydrochloric acid. The resin obtained is hard and of high melting point and is soluble in alcohol and acetone, in weak alkalis such as sodium carbonate, borax, and ammonia solution, and in paraldehyde. It is suitable for leather-finishing and for treating felts in the manufacture of hats. Similar resins are obtained from hexamethylenetetramine and mixtures of *o*- and *p*-hydroxybenzoic acids; from 1,3,4-hydroxytoluic acid and paraformaldehyde in the presence of ammonium acetate; and from salicylic acid and benzaldehyde in the presence of ammonia. These products are of yellow to yellowish-red color and in consequence of their solubility in weak

properly prepared so that the amount of free phenol is at a minimum may be used by the majority of persons without any unpleasant results.

^{76a} Potter, Fleet and Damard Lacquer Company, Ltd., British Pat. 169,347, 1920; J. S. C. I. 1921, 40, 780A.

⁷⁷ J. S. C. I. 1914, 975; French Pat. 468,879, May 5, 1913.

⁷⁸ U. S. Pat. 1,286,372, Dec. 3, 1918.

⁷⁹ Chem. Abs. 1918, 12, 410; British Pat. 110,154, 1917.

⁸⁰ British Pat. 141,059, 1920; Chem. Abs. 1920, 14, 2270; note also British Pat. 141,058, 1920. Note also Moureu and Dufraisse, French Pat. 528,498, June 22, 1920.

⁸¹ German Pat. 339,495, 1919; J. S. C. I. 1922, 41, 639A. Note also German Pats. 357,757, 357,758 and 358,401, 1920; J. S. C. I. 1922, 41, 948A.

alkalies can be used as substitutes for shellac. Resinous products are obtained by the action of formaldehyde on *m*-cresotinic acid in alkaline solution at 30° C., on *o*-methoxybenzoic acid in the presence of concentrated sulphuric acid at 100° C., on *o*-ethoxybenzoic acid at 140-150° C. under pressure, and on salicylic acid at 130° C. under pressure; by the action of paraformaldehyde on 2-ethoxynaphthalene-3-carboxylic acid at 100° C. in the presence of acetic acid and concentrated hydrochloric acid; by the action of ethylal on a mixture of *o*-, *m*-, and *p*-cresotinic acids at 130° C. under pressure; and by the action of benzaldehyde on 2-hydroxynaphthalene-3-carboxylic acid at 130°-140° C. under pressure in the presence of zinc chloride.

Benzoic, salicylic or other easily fusible acid, when stirred into a mixture of phenols, soaps and aldehydes that has been heated until it becomes a viscous mass, serve to arrest polymerization at the gummy stage. The mass is cast in molds and is then subjected to hardening treatment. For example, 2-3 per cent of salicylic acid is added to the gummy mass obtained by heating 100 parts of crude carboic acid, 50 parts of soft soap, and 100 parts of formalin, and the product is cast in molds. The resulting mass remains soft for more than six months, and may be used as a substitute for vulcanite.⁸²

Fusible phenolic products are hardened by McCoy⁸³ by mixing with catechol, tannin and paraformaldehyde and molding the mixture under heat and pressure to decompose the paraformaldehyde with liberation of formaldehyde to effect the desired hardening.

The condensation product of a phenol and an aldehyde may be treated, during or after its formation, with hydrogen, preferably at elevated temperatures and under pressure, in the presence of any of the usual metallic catalysts, e.g., reduced nickel or colloidal nickel, platinum, or palladium. For example, hydrogen is passed at 80° C. and under 3 atm. pressure through the anhydrous liquid condensation product obtained from phenol and a 40 per cent aqueous solution of formaldehyde, in the presence of ammonia, until no further absorption of gas occurs, finely divided nickel being used as a catalyst. The product is filtered, washed, and concentrated. On heating it becomes hard, and is then soluble in alcohol, acetone, and caustic soda. It is odorless and has a higher melting point than that of the resin obtained under the same conditions without hydrogenation. Similar products may be obtained by passing hydrogen through a solution of resins (obtained from aldehydes and phenols) in suitable organic solvents not containing double linkings, e.g., alcohol, in the presence of finely divided nickel.⁸⁴

When potassium or sodium bromide are present in condensing cresol and formaldehyde a product is obtained which does not require any filler. It may be machined in various ways without splintering, resembling celluloid in this respect.⁸⁵

Purified resins are obtained by Coralex from the crude condensation products of phenols and aldehydes by successive washing with hot water, dilute mineral acid, and cold water.⁸⁶ The products are converted into insoluble products by heating to 100° C., or they may be dissolved in alcohol, acetone, amyl acetate, etc., with or without addition of mineral colors to form varnishes or lacquers; or by adding dyestuffs they give preparations suitable for finishing fabrics. The purified resins combine with bases, such as lime, baryta, ferric oxide, etc., or with polyvalent alcohols such as glycerol, or with mixtures of bases and glycerol. The resulting products are hardened by heating to 100° C.

Anhydrous phenol and monochloronaphthalene are used by Aylsworth⁸⁷ to render molding compositions plastic at relatively low temperatures. The binder

⁸² Wenjacit Ges. m. b. H. German Pat. 351,104, 1915; J. S. C. I. 1922, 41, 720A.

⁸³ Chem. Abs., 1918, 12, 1916; U. S. Pat. 1,269,627, June 18, 1918.

⁸⁴ Koch, Ger. Pat. 354,607, April 13, 1920; J. S. C. I. 1922, 41, 772A.

⁸⁵ Mannesmann, Swiss Pat. 87,046; Kunststoffe 1921, 71.

⁸⁶ Chem. Abs. 1921, 15, 319; British Pat. 148,264, 1919.

⁸⁷ J. S. C. I. 1914, 430; U. S. Pat. 1,090,439, Mar. 17, 1914.

is a fusible phenol-formaldehyde resin and sufficient hexamethylenetetramine is added to cause hardening on heating.⁸⁸

Phenylmethylen Saligenin.

2-Phenyl-1,3-benzodioxan is soluble in all the common organic solvents. It does not dissolve in solutions of alkali and is unchanged even after long boiling with 20 per cent sodium hydroxide solution. When treated with concentrated sulphuric acid, an immediate decomposition takes place with the formation of benzaldehyde and red lumps of resinified saligenin. The product gives no aldehyde or ketone test with sodium hydrogen sulfite, phenylhydrazine or hydroxylamine; it gives no test with hydroxyl group reagents such as ferric chloride or acetic anhydride even after long boiling. On heating 2-phenyl-1, 3-benzodioxan with acetic anhydride and a small amount of concentrated sulphuric acid a saligenin resin is obtained.⁸⁹

⁸⁸ An amorphous substance insoluble in water and not distilling with steam was obtained by Fishman, J. Am. Chem. Soc. 1920, 42, 2288, from o-nitrophenol and formaldehyde.

⁸⁹ Adams, Fogler and Kreger, J. Am. Chem. Soc. 1922, 44, 1131.

Chapter 9.

Applications of Phenol-Aldehyde Resins.

The resins and resinoids of this class have found such extensive application that a detailed account of all the uses of these substances would occupy more space than the present volume permits. The preceding pages have enumerated various applications in an incidental way and information regarding molded articles is furnished in Chapters 24, 25, 26 and 27. A cursory glance suffices to show how wide is the range covered by these products, and in the light of our present knowledge of this subject they bid fair to occupy even a more important place. The number of modifications possible in their manufacture is almost unlimited and the satisfactory results obtained thus far indicate that a much greater development may be expected.

The uses of resins made from phenol or cresol and formaldehyde have been developed to a far greater extent than those made from other aldehydes and other hydroxylated aromatic compounds. Acetaldehyde and furfural have, however, begun to assume a measure of importance in the preparation of resins required in certain directions. Their reactivity is of a different character from formaldehyde. The resins of the phenol-formaldehyde type are utilized mostly in the insoluble infusible form. Fusible resins which do not contain a sufficient proportion of formaldehyde, or the product of combination of an inadequate amount of formaldehyde with the phenol, receive an additional quantity, usually in the anhydrous state. Paraform or hexamethylenetetramine commonly are used. Reactive or thermo-setting resins in liquid, pasty or solid state form the foundation of many technical applications. These may be divided into five classes:

1. Transparent cast products prepared by heating the liquid, pasty or solid reactive resin at atmospheric pressure or at a pressure above atmospheric, forming a hard, insoluble, infusible, transparent, amber-like substance. The heating is carried out very slowly and the temperature increased gradually to avoid the formation of bubbles. Sometimes several months may be required to complete the transformation. The material is used for cigar and cigarette holders, pipe stems, beads and other ornaments and numerous novelties.

2. Varnishes, lacquers and enamels which are solutions of the resin in various solvents. These are applied by coating or impregnating paper, wood, fabric, electric coils and the like and reaction brought about by heating with or without pressure. Thus are formed various protective coatings and electrical insulation.

3. Cements, which are usually prepared by the addition to the varnish mentioned above of a large proportion of filling material in finely-powdered form thus forming soft, plastic, putty-like adhesives. These compositions are used for cementing articles which require considerable resistance to heat. For exam-

ple the bulbs of incandescent lamps are cemented into their threaded bases by means of such material. On baking, the cement is rendered insoluble and infusible.

4. Plastic molding compositions consisting of a fusible resin intimately incorporated with filling material and proportioned with respect to available formaldehyde (or the product of reaction between formaldehyde and phenol in appropriate proportions) in the manner explained above, such that on pressing in a heated mold the composition becomes converted into a shaped article which is insoluble and infusible.

5. Laminated pressboard consisting of layers of canvas or paper impregnated with a fusible resin; the layers being superposed and hot-pressed to form sheets, rods, tubes and a few shapes of simple contour. Heat treatment in this case likewise yields a fairly heat-resistant product.

Infusible Transparent Cast Products from Phenol and Formaldehyde.

Artificial Amber.

Transparent amber-like castings are prepared in a number of shades of color from thermo-setting phenol-formaldehyde resinous products. From the castings, which are blocks of convenient size, are machined pipe stems, cigar and cigarette holders, beads and numerous novelties. These products are hard, fairly tough, thermo-rigid, insoluble in organic solvents and more or less resistant to strong acids and alkalis. The disturbance of structure and the shrinkage occurring in the reaction of these products is sufficiently great compared to that of the same resins incorporated with fillers to make impractical the molding or shaping in closed steel molds under hydraulic pressure. Due to the relatively low degree of elasticity compared with rubber or celluloid, articles of irregular shape, such as those mentioned above in most cases, would be broken in removing from the molds. Furthermore, in order to produce transparent products, it is desirable to effect the transformation from a soluble, fusible solid to an insoluble, thermo-rigid resinoid without disturbing the "structure." Transparent final products have not been satisfactorily prepared by molding a ground solid resin because the "structure," if one may use this term, is disturbed in pulverizing. This disturbance of the structure, which does not occur when the molten resin is poured into molds, decreases or entirely eliminates the transparency of the final completely reacted product. It is true that more or less transparent products have been molded in thin pieces of simple shape, but no practical process has been advanced to produce articles which are equal to the cast and subsequently machined products.

Methods of Making Transparent Products.

Two methods of making transparent cast products are employed in general practice. The first method is carried out as follows: A soluble, fusible resin in either liquid, pasty or solid form, to which any desired dyes or other coloring matters have been added, is subjected to heat with or without pressure and preferably with agitation until the mass commences to solidify. The solidification is permitted to take place

in molds without external heating from this point and the reaction is allowed to proceed until an intermediate product is formed. This intermediate product, which corresponds to Baekeland's "Solid B," is infusible, elastic and swells in phenol and acetone. Due to the fact that this product is solid at all temperatures and will hold its shape it is removed from the mold and may be stored away for future use or may be subjected to the final treatment which consists in heating at a temperature of about 150-160° C. under pressure of about 100 lbs. per square inch. This is accomplished by placing the castings in a closed vessel and pumping in air or some inert gas to obtain the desired pressure. The use of high pressure during the transformation to the final or infusible and insoluble hard product prevents bubbles forming in the mass and permits the use of a considerably higher temperature than could be employed without pressure, thereby shortening the hardening process.

The second method which is used for making these products consists in subjecting the initial soluble and fusible resinous mass to baking at a temperature of about 65° C. until the intermediate product is obtained which, as described in the preceding method, has the property of holding its shape at all temperatures. This operation is carried out in molds to form the desired shape. The intermediate product is then removed from the molds and heated further at atmospheric pressure at a temperature ranging from 50-100° C. for a period of from several weeks to several months, depending on the thickness of the articles to be hardened. Usually after this prolonged heating the products are heated for a short period of several days at a temperature between 125 and 150° C. The higher temperature employed in this step tends to produce a product which is stable in color and has a higher degree of transparency.

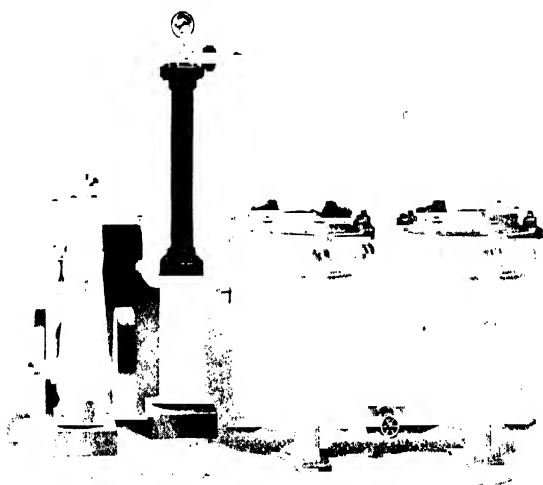
Difficulty has been encountered in obtaining pale yellow products of the type described, and after investigation the conclusion has been reached that the less these products are exposed to air or oxidizing gases during the hardening process, the lighter will be the color of the final product. For this reason, when the hardening process is carried on under pressure, it has been found desirable to use an inert gas rather than air. It is possible in preparing the transparent products to add substances such as fish scales and powdered mica to produce a shimmering effect on the surface of the article; to add waxes for the purpose of producing a cloudy amber effect, and dyes of many different colors for producing material suitable for beads and various novelties.

Varnishes, Lacquers, Enamels and Electrical Insulating Mediums.

Varnishes.

Varnishes consisting of liquid fusible resins either with or without solvents are employed for coating wood, metal and other materials and are also used for impregnating wood, paper and cloth to serve as pro-

protective coatings for resisting moisture, acids, alkalis and all solvents. In certain cases where the coated products are to be subjected to shock which mechanically crack or chip the resinous coating, high boiling solvents which are immiscible with water and form so-called "solid solvents" for the infusible resin are added. Naphthalene, anthracene, xylol and toluol, nitrobenzol or nitrotoluol, camphor oil, terpenes and high-boiling point ketones have been used for this purpose as well as some of the natural resins or permanently fusible phenol-formaldehyde resins; for example, ortho cresol resin. When the varnish is to be



Courtesy of Buffalo Foundry & Machine Company.

FIG. 5.—Vacuum-Pressure Impregnating Kettles. The material to be impregnated is placed in the middle container and is dried under vacuum. The right-hand container is filled with a solution of the resin used for impregnation. Upon opening the connecting valve between the two vessels the solution floods the middle vessel. Air pressure can be applied to force the solution into the pores of the material which is being impregnated.

used for coating metal or other materials low-boiling-point solvents are often used for the solid phenol-formaldehyde resins. Alcohol and acetone are commonly used for this purpose and the resulting solution is applied either by dipping, brushing or spraying the articles to be coated. The products treated are then usually dried at a low temperature to expel the solvent and a second and possibly a third coat applied in the same manner with subsequent drying. Finally the articles are baked at a temperature of 65-70° C. and the temperature gradually raised to about 125-150° C.; the baking extending over a period of 5 to 8 hours. The baking time may be reduced considerably by placing the articles in a closed container and applying a pressure of 75-125 lbs., at which pressure a higher temperature of 125° C. can safely be employed. When the liquid phenol-formaldehyde resin is employed as a

varnish, for instance, for impregnating wood, cloth, etc., the articles to be impregnated are dried under vacuum and the vessel containing the articles is then flooded with the liquid resin. A pressure of 100-150 lbs. is applied to force the resin into the pores of the wood or other material, and after the pressure treatment, which usually requires 1 to 3 hours, the articles are removed, drained and gently heated at a temperature of about 65° C. until the reactive resin has gelatinized or formed the intermediate product. Finally the impregnated articles are either baked at a gradually rising temperature between 65-150° C. for a long period, or they may be subjected to a higher temperature of 150-160° C. in a closed vessel under pressure. The use of an external pressure in this way prevents the formation of bubbles from volatile matter and insures the material being free from air holes or porous spots.

The products which have been impregnated with phenol-formaldehyde resins and subsequently baked to form the infusible or final product may be machined and polished to form articles which will have properties similar to the molded products prepared from these resins. For example the handles of nail brushes which are subjected to hot water and soapsuds have been prepared from these products and combine the necessary resistance under severe conditions with good appearance. Furthermore the high polish and surface lustre is permanently retained by articles treated in the manner described above.

Enamels and Lacquers.

Enamels and lacquers have been satisfactorily prepared from phenol-formaldehyde resins and are used for purposes such as coating jewelry, brass, beads, polished brass hardware, etc. The enamels are prepared in a manner similar to the lacquers but contain suitable fillers and dyes which give a somewhat tougher surface to the coating and any desired dark color. The drying and baking treatment is the same.

Insulating Mediums.

Insulating mediums for electric coils, dynamo and motor armatures are formed by impregnating the coil or armature with liquid phenol-aldehyde resins and subjecting the impregnated product to heat, with or without pressure, to form a hard moisture- and heat-resisting medium possessing high dielectric strength. In view of the infusibility of the final product obtained from these materials it has been very difficult to repair impregnated coils or armatures, and it has been found necessary to prepare an insulating medium which, although infusible, will be soft enough at high temperatures to cut so that the impregnated coils or armatures can be satisfactorily repaired. For this purpose a solvent of high boiling point, for example naphthalene or anthracene or any similar solvents, may be utilized. These solvents are used in small percentages, seldom exceeding 25 or 30 per cent of the weight of the resin and usually being present in a considerably

smaller proportion. The resulting product after the heat treatment, which is similar to that described above for impregnation of wood and other materials, is a substance which, while hard at room temperature and possessing high dielectric strength, is soft and elastic at a temperature of about 125° C.

Antiseptic Paint.

One of the earlier specific applications of phenol-formaldehyde condensation products is that of Horn¹ for making antiseptic and antifouling paint. Two parts each of phenol and formaldehyde (40 per cent solution) and 1 part of hydrochloric acid are heated to yield a resinous product slowly soluble in turpentine.

Varnishes.

Backeland² prepares a varnish by condensing phenol and formaldehyde in the presence of a base such as ammonia, caustic alkalis, carbonates, alkali sulphides, acetates, cyanides, and trisodium phosphate, borax or soaps. Water is separated and the resinous product dissolved in a solvent, such as alcohol or acetone. The base may not exceed one-fifth of a mol. to each mol. of the phenolic body employed. Formaldehyde may be used in widely varied proportions. In an example, equal amounts of phenol and 40 per cent formaldehyde are employed. Heat converts this product to an infusible, insoluble, resin. Backeland³ also prepares a varnish comprising a condensation product of phenols and formaldehyde substantially free from uncombined phenols, together with a solvent containing a readily volatile organic liquid (e.g., acetone) and another organic liquid (e.g., amyl alcohol) miscible with the first but immiscible with water, having a higher boiling point than water, and volatilizable without decomposition when heated at ordinary pressures.

Jones⁴ obtains varnishes and paints by using a solution of the resin in aniline or its homologues and a hydrocarbon such as xylol. A solution of 140 parts condensation product in 75 parts aniline and 85 parts xylol is said to be superior to alcohol solutions in penetrating power. The solution dries with sufficient rapidity and adheres well to the surface coated. Colors and pigments may be added.

An alcohol-soluble phenolic condensation resin put out under the name of "Shellackose" appears as a yellowish powder, one part of which dissolves in about two parts of alcohol. The solution is turbid but clears on standing. The solution is neutral and may be used for lacquering purposes. "Shellackose" dissolves in aqueous caustic soda solutions and advantage is taken of this to make leather finishing compositions. One formula recommended is to stir 20 parts of "Shellackose" into a solution made from 90 parts of water and 8½ parts of 90° Bé. caustic potash. The mixing is carried out at a temperature of about 80° C. Such a solution suitably diluted and colored with black dye (e.g., nigrosine) affords a leather finishing composition. "Shellackose" lacquers and bronzing liquids dry readily and afford a brilliant surface. They are made by dissolving the resin in alcohol using proportions of one part resin to one or two parts alcohol. After standing for a time to clarify, the clear liquid is decanted and used. The dried lacquer is not affected by benzine, varnish makers' naphtha, benzol, turpentine, etc. "Shellackose"⁵ has been proposed as a primer for wood, masonry and concrete structures. A phenol-formaldehyde condensation product called "Medolit"⁶ is recommended by Bottler for use in polishes and as a substitute for shellac varnish.

¹ U. S. Pat. 898,476, Sept. 15, 1908.

² U. S. Pat. 954,666, Apr. 12, 1910.

³ U. S. Pat. 1,018,385, Feb. 20, 1912; J. S. C. I. 1912, 347.

⁴ U. S. Pat. 1,200,731, Oct. 10, 1916.

⁵ For further particulars, see Bottler, *Kunstharzen*, Munich, 1919.

⁶ Gesellschaft für Teerverwertung in Duisburg-Meiderich.

Coated Articles.

Various procedures are known for coating wood, articles of cement or plaster of paris, etc., with phenol-formaldehyde condensation products. Space does not permit the consideration of these in detail. Wood veneering processes have been developed by Aylsworth,⁷ McClain,⁸ and Buffum.⁹ Backeland¹⁰ has applied phenolic condensation products to the coating of concrete. Jones¹¹ has devised special methods of securing good adherence of such coating on metal. Kempton¹² provides a method of coating electrical condensers. Horn,¹³ Ellis,¹⁴ Collardon¹⁵ and Heinemann¹⁶ utilize phenol-formaldehyde condensation products in making antifouling paints for ships. Beatty¹⁷ coats moving-picture film with a condensation product of an aldehyde and a phenolic derivative. To obtain better adhesion, Matheson¹⁸ applies to the surface to be coated, a layer of nitrocellulose, then a coating of a phenol condensation product dissolved in a solvent common to both. This insures good adhesion. Artificial leather, aeroplane wings and other fabrics coated with nitrocellulose are rendered less inflammable by an outer coating of the phenolic resin. To prevent shrinkage of protective coatings applied to machinery, Backeland¹⁹ adds a filler, e.g., graphite, clay or iron oxide. Leather impregnated with a phenolic condensation product and heated to 100-150° C. to harden the resin is stated by McIntosh²⁰ to be hard, tough and close-grained and to possess good electrical insulating properties. Backeland²¹ coats the interior of metal cans with a fusible resin of the phenol-formaldehyde type and the temperature is raised to 130° C. or over to transform the coating to an infusible layer. The container is intended to be used in packaging food products.

Metal Coatings.

Protective coatings for iron and steel are prepared by Townsend²² from phenol and formaldehyde by an ingenious process. The phenol and formaldehyde, or a reaction product of these substances, in solution in an appropriate solvent, for example alcohol, receives an addition of a metallic salt which is soluble in the particular solvent employed.

⁷ U. S. Pat. 1,139,470, May 18, 1915.

⁸ U. S. Pat. 1,299,747, Apr. 8, 1919.

⁹ U. S. Pat. 1,197,601, Sept. 12, 1916.

¹⁰ U. S. Pat. 1,160,363, Nov. 16, 1915.

¹¹ U. S. Pat. 1,171,725, Feb. 15, 1916.

¹² U. S. Pat. 1,249,770, Dec. 11, 1917.

¹³ U. S. Pat. 898,476, Sept. 15, 1908.

¹⁴ U. S. Pat. 944,420, Dec. 28, 1909.

¹⁵ German Pat. 274,875, Jan. 19, 1913; U. S. Pat. 1,105,619, Aug. 4, 1914.

¹⁶ British Pat. 11,394, 1914; U. S. Pat. 1,176,056, Mar. 21, 1916.

¹⁷ U. S. Pat. 1,158,963, Nov. 2, 1915.

¹⁸ U. S. Pat. 1,309,581, July 8, 1909.

¹⁹ U. S. Pat. 982,230, Jan. 24, 1911.

²⁰ U. S. Pat. 1,269,292, June 11, 1918.

²¹ U. S. Pat. 957,137, May 3, 1910.

²² U. S. Pat. 1,146,214, July 13, 1915.

In the present example cupric chloride is suitable. A dark red or brown solution is formed which is quite stable. On applying this solution to clean surfaces of iron or steel, the reduced metal, e.g., copper, is precipitated as a film on the iron or steel surface and ferric chloride is formed, which serves as a condensing agent to harden the resinous coating. Townsend²³ also uses the same method with toxic salts, such as copper or mercury salts, to obtain an antifouling coating.²⁴

In coating metal and other surfaces with phenol-formaldehyde resins (such as Bakelite) and asbestos, blistering is prevented by coating the surface with the resin, applying asbestos paper, hardening the resin by heat, and then impregnating the asbestos with liquid or dissolved resin which is finally hardened.^{24a}

Ruff^{24b} utilizes an aqueous alkaline solution of phenol-formaldehyde resin for lacquering metals. Ruff mixes three kilos of 30 per cent formalin, one kilo of cresol and one litre of 8 per cent caustic soda solution and heats until a sample on cooling is quite viscous. Additional caustic soda solution is added to form a clear liquid composition. The well-cleaned metal articles are coated with this composition and after drying are heated for 6 hours at 90° C. Hardening takes place more quickly at a higher temperature but the lacquer does not adhere as well.

Indurated Wood.

Phenolic condensation products may be separately prepared and wood impregnated with this material,²⁵ or phenol and formaldehyde are absorbed by wood and synthesis brought about by heating.²⁶ Aylsworth²⁷ obtained an indurated product by soaking wood in a solution of hexamethylenetetramine and then impregnating with a fusible phenolic resin. On heating, an infusible condensation product is formed. Dyer²⁸ uses indurated wood in making battery wells.

Wood Finishing.

A coating of a phenolic condensation product is applied to wood and the surface is hot-pressed to secure a smooth glossy finish or an embossed effect.²⁹

Aylsworth³⁰ dries wood for several hours at 105° C. or a higher temperature, and then coats it with a phenolic varnish containing ingredients in proportions to form a final infusible condensation product.

²³ U. S. Pat. 1,273,954, July 30, 1918.

²⁴ According to Holzverkohlungs-Ind. A.-G. (German Pat. 337,061, Mar. 13, 1919; J. S. C. I. 1921, 602A) the condensation products of phenol and formaldehyde, produced by either acid or alkaline catalysts, when heated with a mercuric salt yield a yellow product, soluble in caustic alkalies but insoluble in alkali carbonates, water and the usual solvents. These products are used for disinfecting and antiseptic purposes.

^{24a} Wirth, British Pat. 171,369, 1921.

^{24b} German Pat. 304,985, June 30, 1917.

²⁵ Baekeland, U. S. Pat. 942,852, Dec. 7, 1909.

²⁶ Baekeland, U. S. Pat. 949,671, Feb. 15, 1910.

²⁷ U. S. Pat. 1,111,286, Sept. 22, 1914.

²⁸ U. S. Pat. 994,067, May 30, 1911.

²⁹ Baekeland, U. S. Pat. 1,019,408, Mar. 5, 1912.

³⁰ Chem. Abs. 1915, 1849; 1918, 1839; U. S. Pat. 1,139,470, May 18, 1915.

The varnish is applied at a temperature somewhat less than that of the wood and the coated material is then baked at a temperature lower than that used for drying until the coating is rendered insoluble and infusible.

Insulation.

Baekeland³¹ utilizes for insulating purposes a fluid phenol-formaldehyde condensation product, with or without a plasticizing agent, capable of forming an infusible resin on heating. He makes coils for electrical uses³² with the windings in spaced relation, the spaces or interstices being impregnated with the condensation product. The coils are then heated under pressure to effect transformation *in situ*, into an insoluble and infusible resin. This serves as a support and insulator for the windings. A method of coating or impregnating electrical conductors with an infusible phenol-formaldehyde resin is that of bringing formaldehyde into contact with the article previously coated or impregnated with a fusible resin. Absorption of the formaldehyde and subsequent exposure of the treated material to heat brings about transformation to an infusible substance. The treatment may be carried out in a non-oxidizing atmosphere. The resin may have incorporated with it a plasticizing agent such as eugenol, nitro or chlornaphthalene.³³ Jackson³⁴ hardens a phenol-aldehyde resinous condensation product which is applied to fabric coverings of coils for electrical insulation purposes, by heating under pressure, then drying at a lower temperature *in vacuo*, and after applying a further quantity of the condensation product, the hardening process is completed by further heating for several hours at a higher temperature in a closed vessel under air pressure.

Miscellaneous Insulating Applications.

Spark coils for internal combustion engines are effectively insulated by Bakelite.³⁵ Magnètic wedges, employed by Frederick and McCullough³⁶ in the slots of dynamos, are built up by means of phenolic condensation products. Scheibe,³⁷ Halbleib and Lee,³⁸ and Zenk³⁹ employ the material in commutator construction. Aichele⁴⁰ uses it

³¹ U. S. Pat. 1,213,144, Jan. 23, 1917. The application of bakelite in the manufacture of electrical insulation is described by Bültemann, *Kunststoffe*, 1922, 12, 66 and 76.

³² U. S. Pat. 1,213,726, Jan. 23, 1917.

³³ Aylsworth, U. S. Pat. 1,047,484, Dec. 17, 1912.

³⁴ J. S. C. I. 1920, 73A; U. S. Pat. 1,323,284, Dec. 2, 1919.

³⁵ Apple, U. S. Pat. 1,132,297, Mar. 16, 1915.

³⁶ U. S. Pat. 1,231,588, July 3, 1917.

³⁷ U. S. Pat. 1,241,559, Oct. 2, 1917.

³⁸ Chem. Abs. 1918, 1950; U. S. Pat. 1,274,411.

³⁹ Electrical Rev. 87, 836; U. S. Pat. 1,046,928, Dec. 10, 1912, and 1,255,681, Feb. 5, 1918.

⁴⁰ U. S. Pat. 1,296,731, Mar. 11, 1919.

for insulating sleeves. A composition increasing in electrical resistance or disruptive strength with increase in temperature is obtained by Hayden ⁴¹ from a mixture of paraffin oil and a phenolic resin. He dissolves the oil in amyl acetate and the resin in alcohol, which solvents are miscible. The proportion of solvents must be carefully controlled to avoid precipitation of either oil or resin. When the solvent has evaporated a product of the consistency of soft rubber results. It may be applied to fabrics to produce a flexible insulating cloth.

Cements.

Cements for electrical insulating purposes, joining glass, porcelain, metal and other surfaces have been prepared from liquid, pasty or solid reactive resins and fillers such as asbestos flour, flint and other substances. These are prepared in semi-liquid form and also in a solid but thermo-plastic form. Preferably they are applied to heated surfaces and subsequently are subjected to a prolonged baking at a gradually rising temperature from 65-150° C. Other substances, such as natural resins, have been added to cheapen or give the desired properties to these products; for example a mixture of equal parts of rosin or resinate and a thermo-setting resin has been used as a cement in the manufacture of electric light bulbs. This cement is used to join the metal base to the glass.

These cements are prepared usually by mixing the reactive resin and filler together either on heated mixing rolls or in a heated masticator of the type shown in Fig. 30. The liquid cement for use in cementing bristles into brushes, making a gas-tight joint in between the metal electrode and porcelain in spark plugs, cementing together porcelain insulators, cementing the handles of surgical instruments, carving knives, etc., has a combination of properties which is not found in other cements. The infusibility, water resistance and strong adhesive properties makes it invaluable.

Baekeland ⁴² has made use of these resins as adhesives. The surfaces to be joined are treated with a cement composed of such products of the partial condensation of phenol and formaldehyde as are capable, when hardened, of yielding insoluble infusible substances. These condensation products may be dissolved in a solvent, and an addition of a filling material made to reduce the strain of shrinkage of the final product. A method given by Baekeland for preparing the cement is to heat (under a reflux condenser for ½ hour) a mixture of phenol 100 parts, 40 per cent formaldehyde solution 90 parts and caustic soda 5 parts, dissolved in minimum amount of water. The liquid product may be boiled to a heavier body. To 3 parts of the reaction product, 2 parts of a filler, e.g., ground flint or emery, are added. Baekeland and Thurlow ⁴³ also used this material for uniting veneer to wood.

⁴¹ U. S. Pat. 1,096,839, May 19, 1914.

⁴² J. S. C. I. 1912, 347; U. S. Pat. 1,019,407, Mar. 5, 1912.

⁴³ U. S. Pat. 1,019,408, Mar. 5, 1912.

Brown⁴⁴ employs phenol-formaldehyde resinous substances as a cement for joining rubber to other materials such as metal or wood. Egerton⁴⁵ impregnates a layer of fabric with the phenol resin and uses this as a medium for uniting vulcanized rubber and other articles by mildly heating to effect the union. Pipe cements have also been prepared from phenolic resins by Aylsworth.⁴⁶ Hayhurst⁴⁷ seals the joints between the tiles forming the lining of a vessel for acids, and other liquids by molding into them plastic phenolic material and then subjecting the whole lining to an increased temperature. A filler, such as asbestos, may be employed.

The Adhesives Research Committee⁴⁸ has tested phenol-formaldehyde condensation products for cementing wood. Unsatisfactory results were obtained when the cementing agent was made from equimolecular proportions of phenol and formaldehyde. When an excess of phenol was employed the resulting resin was more elastic and could be used in admixture with camphor or even gelatin. The adhesive was prepared as follows: 100 parts of phenol were heated with 50-80 parts of 40 per cent formaldehyde solution, employing a reflux condenser. A small quantity of catalyst in the form of a mineral or organic acid or base was added. The heating was continued for 8-10 hours. The liquid was evaporated in an open vessel to the consistency of a thick syrup. Ammonia solution then was added and the heating continued for a short time to drive off the bulk of the ammonia. The adhesive so obtained possessed the consistency of ordinary glue solution at the same temperature and was capable of being applied by brush or heated rolls. Tests of its adhesive qualities showed it to compare with a good grade of glue.

Molding Compositions.⁴⁹

Impregnation of Filler.

•The filling material, which is usually wood flour, should be thoroughly and uniformly impregnated with the resin. This may be accomplished in two ways: by mixing a solution of the resin with the filler, or by incorporation of the dry resin with a filler on hot rolls. Impreg-

⁴⁴ U. S. Pat. 1,250,959, Dec. 25, 1917.

⁴⁵ U. S. Pat. 1,353,800, Sept. 21, 1920.

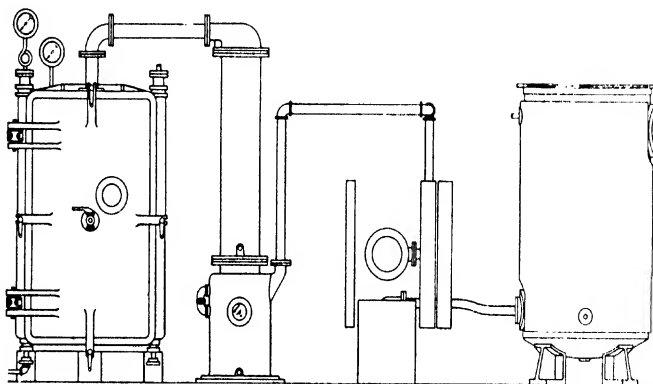
⁴⁶ U. S. Pat. 1,065,495, June 24, 1913.

⁴⁷ British Pat. 122,661, Oct. 26, 1917.

⁴⁸ Chem. Age, London, 1922, 7, 207.

⁴⁹ See Chapters 24, 25, 26 and 27. The author deems unnecessary any reference to a considerable number of articles appearing in the literature which constitute merely reviews or "write-ups" of Bakelite and similar products. However, the reader may be interested in the following: Clément and Rivière, *Chimie et industrie* 1922, 8, 38, furnish a brief description of the preparation of Bakelite. This product is reviewed by Marcia, *Ann. chim. sci. ind.* 1920, 54, Matsumoto, *J. Chem. Ind. (Japan)* 18, No. 207; *Chem. News* 1915, 112, 195; *J. S. C. I.* 1915, 1104 has investigated the conditions of formation of phenol-formaldehyde resins. Eller, *Chem. Abs.* 10, 1277; *Kunststoffe* 6, 45, and Caffignier, *Chem. Abs.* 12, 96, also summarize the work done in this field and

nation by means of a solution of the resin is carried out by breaking the slabs of resin into coarse fragments and tumbling with alcohol in a drum similar to that used for cutting shellac. About 10 per cent of hexamethylenetetramine based on the weight of the resin employed is added and the solution obtained may, if necessary, be strained to remove any coarse particles. It is then thoroughly mixed with the wood flour filler, usually equal parts of resin and filler being employed. This product is dried to eliminate the solvent and then is ground. As batches of resin vary considerably in quality it is desirable to select a quantity from several lots in making up the charge of resin to be dissolved in alcohol. Or several batches of finished molding powder may be mixed in a tumbling drum. This procedure tends to equalize unavoidable lack of uniformity in the resin.



Courtesy of J. P. Devine Company.

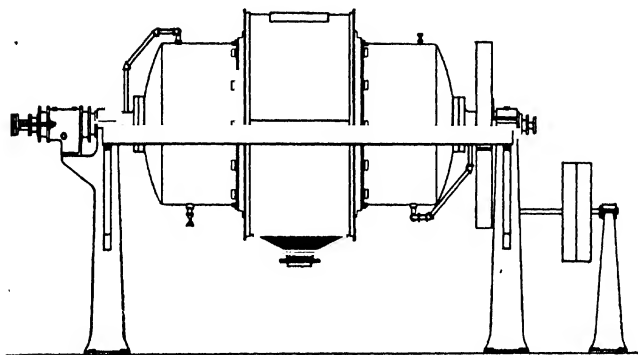
FIG. 6.—Vacuum Shelf Dryer for use in removing solvents in the preparation of molding compositions.

Impregnation on Rolls.

Differential rolls (Fig. 27) such as are used in rubber compounding are heated to a temperature at which the resin is in a soft plastic state and the resin, wood filler and hexa are incorporated on these rolls in much the same manner as rubber is mixed with filling material. Too

a tabular review of patents is given by Kaurch, *Kunststoffe*, 4, 268; *Chem. Abs.* 1914, 3244. The patents on Bakelite are discussed as a case of double patenting by Ephraim, *Kunststoffe* 1922, 12, 2, leading to a rejoinder by Scheiber and Hamburger, *ibid.* 1922, 12, 41. The discussion is continued by Ephraim, *ibid.* 58. See also Editorial, p. 87. Flight, *Beama*, Dec., 1921, 542, discusses phenol-formaldehyde resins from the standpoint of the electrical industry. Daniels, *Machinery*, Sept., 1922, 14, describes methods of using molding compositions in use at the plant of the Shaw Insulator Co., Newark, N. J. Insulators from synthetic resins and asbestos, *Neueste Erfind u. Erfah.* 1920, 47, 14; *Chimie et industrie* 1921, 5, 73. This is a review of the properties and uses of Bakelite and especially of the preparation of electrical insulators from Bakelite mixed with 60-70 per cent of asbestos.

protracted a heat treatment on the rolls will cause the resin to thicken or set, and this should be avoided especially when molding compounds having good flowing qualities in the mold are desired. Fluxes such as aniline, benzyl alcohol, chlornaphthalene, etc., may be added at this stage. Also, if a mold lubricant such as stearic acid or wax is employed, this material may be added on the rolls. Ordinarily only a very small proportion, say 1 or 2 per cent of the total batch, of flux or lubricant is required.



Courtesy of J. P. Devine Company.

FIG. 7.—Rotary Vacuum Dryer, sometimes called a "Carbonator," adapted for drying molding compositions. The rotary drum is jacketed for steam or hot water heating, balls are placed in the drum and these serve to mix and grind the composition. A vacuum pump, condenser and expansion tank (see Fig. 6) are used in conjunction with this dryer.

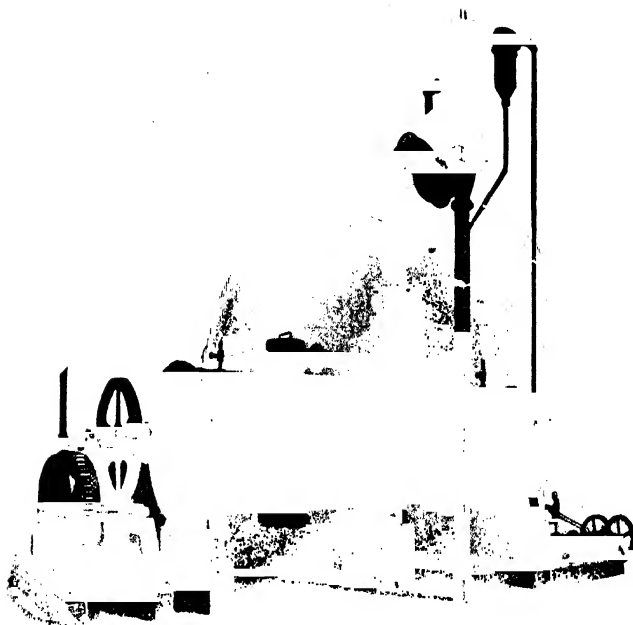
Resinous Solutions for Paper.

In manufacturing the resin in liquid form to be used in impregnating sheets of paper, cloth, etc., which are to be pressed together to form stiff sheets and blocks it is desirable to react the phenol and formaldehyde in about molecular proportions at a considerably lower temperature and pressure, adding enough aqueous ammonia to form the requisite quantity of hexa. When ammonia is added to the formaldehyde considerable heating takes place and this reaction should be allowed to subside before heat is applied to the digester to bring about the reaction. In fact when the ammonia is added it is desirable to cool the digester. The reaction may be carried on for about an hour at between 90 and 95° C., then water is boiled off *in vacuo*. A solution prepared in the manner described above for the impregnation of wood flour will keep only a short time; ordinarily it should be used within 24 hours. The reaction at high temperatures appears to make a more sensitive resin which in the presence of hexa quickly thickens in solution to a jelly-like material. That made at lower temperatures with the addition of ammonia affords a product which will retain its consistency for several months.

Acetaldehyde Resin.

For varnishes a more stable product is obtained by using acetaldehyde. This aldehyde together with phenol is heated in a copper digester, a small amount of sulphuric acid being added as a catalyst and the reaction being carried out at 135-140° C. A solution of this resin in alcohol or other solvent and containing the requisite addition of hexa affords a very stable varnish solution.

Baekeland⁵⁰ calls attention to the general use of wood fibre as a filler. This material even after drying contains water which can be



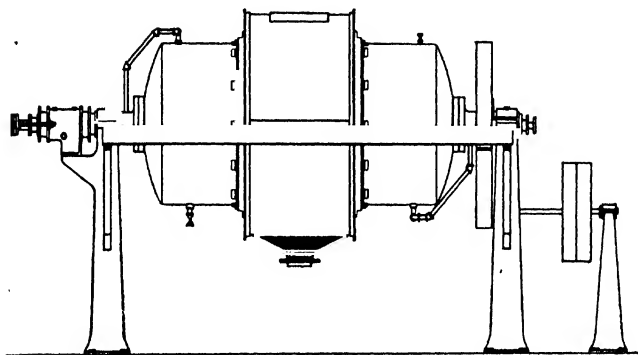
Courtesy of Buffalo Foundry & Machine Company.

FIG. 8.—A combination mixer and rotary vacuum dryer adapted for preparing molding compositions. It is jacketed for heating and the solvent is removed from the composition in vacuo.

set free by heating at somewhat higher temperatures. The same is true of cotton and paper. Yet these materials make good insulators. Baekeland observes that insulating results depend upon the condition in which the water is present. Unduly large amounts of ammonia in the presence of wood fibre act in some way to lessen its dielectric properties. Ammonia seems to fasten itself on the wood fibre, and, according to Baekeland, possibly decomposes some of the substances contained in the fibre, thereby attracting water which previously was

⁵⁰ J. Ind. Eng. Chem. 1916, 570.

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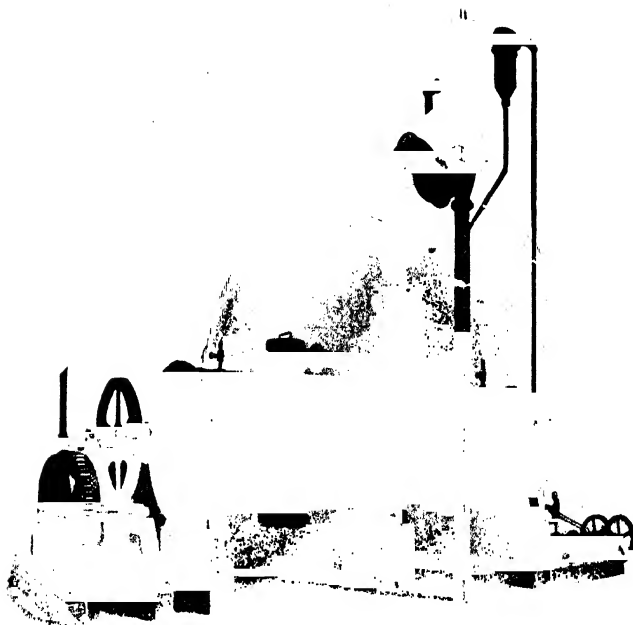
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⁵⁰ J. Ind. Eng. Chem. 1916, 570.

The anhydrous resin is prepared from raw materials in proportions which supply at least two phenolic groups to each methylene group. The hexa is used in quantity sufficient to furnish approximately equimolecular proportions of methylene and phenolic groups. The mixture is subjected to a quick molding operation and the shaped article is heated to render it hard and infusible.

Irregular Shapes.

The production of molded articles of irregular shapes sometimes offers difficulty because the molding composition does not flow well into the various parts of the mold. Brown⁵⁶ produces molded articles of a composite nature by shaping molding composition about inserts of fibrous materials which have been coated or impregnated with reactive phenol-formaldehyde resin.

Phonograph Record Blanks.

Bakeland⁵⁶ applied phenol-formaldehyde condensation products as a binder in the manufacture of phonograph records and obtained a disc which was very hard and strong. Shellac ordinarily is used as the binder for a mineral filler in making phonograph records and continues to be used despite the efforts made to displace it by synthetic resins. The manufacture of phonograph records from shellac has become so standardized that the substitution of synthetic resins would involve a material departure from present practice and operating technique and also a substantial investment in new equipment. Although better records can be made from synthetic products, the commercial application of the latter has been taken up only in a limited way by a small number of concerns. Shellac has yet to be displaced by synthetic resins which in some respects at least have decidedly more attractive properties. The hardness and toughness of shellac and the simplicity of molding records containing it, under the present standardized methods, place before the synthetic resin chemist a hard problem to solve if he would bring forth a synthetic material acceptable, in lieu of shellac, to record manufacturers. Aylsworth⁵⁷ developed several methods and compositions for making phonograph records from phenol-formaldehyde condensation products. A backing of cheap material is coated with a fusible phenol resin and a fluxing agent is added to increase plasticity. Chlornaphthalene, m-dinitrobenzene, nitronaphthalene, camphor or stearamide serve as plasticizing agents. Edison⁵⁸ uses a mixture of the resin and wood pulp. Beatty⁵⁹ reacts on phenol with acetone in the presence of an acid to produce, in all probability, the compound dioxydiphenyldimethylmethane. This substance is treated with formaldehyde and a resin⁶⁰ obtained which is mixed with

⁵⁶ U. S. Pat. 1,308,330, July 1, 1919.

⁵⁷ U. S. Pat. 1,083,264, Dec. 30, 1913.

⁵⁸ U. S. Pats. 1,071,685, Sept. 2, 1913; 1,110,417, Sept. 15, 1914; 1,146,388, July 13, 1915; note also 1,043,389; 1,060,577; 1,061,258; 1,092,512; 1,146,384; 1,146,385; 1,146,386; 1,146,387; 1,146,389; 1,146,390; 1,146,391; 1,151,849; 1,167,468; 1,170,391; 1,230,816; 1,255,500; and 1,283,450.

⁵⁹ U. S. Pat. 1,146,413.

⁶⁰ U. S. Pat. 1,158,964, Nov. 2, 1915.

⁶⁰ Concerning use of phenol-furfural resins see Novotny, U. S. Pat. 1,398,148, Nov. 22, 1921, relating to phonograph records and 1,398,147 on the production of a moldable composite body.

fillers and molded into records. Phonograph records also are made of fibrous layers impregnated or covered with phenol-formaldehyde resin.⁶¹ The layers are placed together and pressed in a heated mold under a die by means of which the sound trace is impressed. This treatment results in a finished product which is hard and infusible.

In making sound records Novotny^{61a} prepares a fusible phenol-acetaldehyde resin using hydrochloric acid as a catalyst. This is dissolved in alcohol to form a thin solution and hexa is added. Sheets of fibre are impregnated with the solution and subsequently heated to remove solvents and partially react the resin thus preventing side flow during hot pressing. A plurality of sheets are cemented together with the resin solution and subjected to heavy pressure to insure firm adhesion. This product is coated with a thick paint composed of barium sulphate and resin solution. The blanks are heated to 250° F. for about 1 hour, coated a second time with the resin, dried to remove solvent and hot pressed in a record mold.

Printing Plates and Matrices.

The development of processes of making infusible resins by hot-pressing has been accompanied by much earnest endeavor to produce printing plates and matrices for use in the casting of stereotype and similar plates commonly employed in the art of printing. Aylsworth,⁶² in 1914, described a method of making printing plates from phenol-formaldehyde condensation products. Baekeland⁶³ has used paper or a fibrous material impregnated with a phenol resin which is capable of taking an impression from the type and of subsequently being transformed by heating into an infusible form which can withstand the action of molten type metal. During a number of years past, no small measure of experimental work has been brought to bear on the problem. According to Redman, Weith and Brock,⁶⁴ in making plates from phenol resins the original zinc etching is placed on the top of a sheet of the resin compound which has been previously heated until soft and pliable, and both are gradually pressed in a hot press up to a pressure of about 2000 pounds per square inch. The press heads are prevented from coming together by means of controlling bars, while the plastic compound is allowed to flow out around the edges. After hardening for a few minutes, the mold is removed, and may be used immediately for the production of positive plates in the same way from fresh plastic sheets. A layer of oiled paper, metal foil, or talc dust, etc., is used to prevent the cast from sticking to the mold.

Matrices are commonly prepared by impregnating paper with condensation products of phenols and formaldehyde, and molding the matrix therefrom, the resin being rendered infusible either during or

⁶¹ Rommler, British Pat. 174,372, 1922. Chem. Abs. 1922, 16, 1842.

^{61a} U. S. Pat. 1,440,097, Dec. 26, 1922.

⁶² U. S. Pat. 1,098,610, June 2, 1914, and 1,144,338, June 22, 1915.

⁶³ U. S. Pat. 1,233,298, July 17, 1917.

⁶⁴ J. Ind. Eng. Chem. 1917, 9, 388; J. S. C. I. 1917, 512.

after the operation of molding. Williamson⁶⁶ first saturates a heavy blotting paper with a 25 per cent solution of silicate of soda, presses to remove excess of the solution and dries the sheets. These, when dry, are still highly absorbent and are further impregnated with a phenolic resin. Two or three treatments may be necessary to load the paper with the requisite amount of resin. The sheet is dried at 70° C. and is given a backing of strong thin paper. The other side is polished or faced with onion-skin paper. The sheet is now molded in the press by forcing it against the type to be reproduced. With the mold at 180° C. the sheet is held in the press about 1 minute, then is removed and placed on a hot plate for a short time to complete the hardening operation. The advent of cheap furfural, by processes described in Chapter 11, has given a stimulus to the production of plates and matrices from phenol-furfural resins and the prospective low cost of furfural gives this line of research a decided ring of promise.⁶⁶

Molded Pulp.

Peabody⁶⁷ incorporates phenolic condensation products with paper pulp in the beater engine. The pulp then is dried and molded. A phenol-formaldehyde resin is incorporated by Baekeland⁶⁸ with paper pulp and after thorough mixing the product is pressed into any desired shape and heated sufficiently to render the resin infusible. From 15 to 50 per cent of the phenol-formaldehyde resin is used. Knife handles, buttons and similar articles may be made from this composition. Juchli⁶⁹ also employs paper pulp.

The use of corn cobs as an insulating material and filler is recommended by Darling⁷⁰ in conjunction with phenol-aldehyde resins.

Impregnated Paper and Canvas. Laminated Pressboard.

In the electrical field it has been common practice to coat paper with varnish or solutions of resins and to compact the sheets to a solid plate or block by hot pressing. Materials made in this manner are called "micarta." Shellac, copal and other natural resins have been used in making this product. Of the natural resins copal and shellac yield pressboard possessed of good mechanical and electrical properties when cold, but on account of softening when heated to 70-90° C. the mechanical strength and to a large extent also the electrical strength are lost when a temperature of 80° C. is reached. Such temperature conditions are of course not unlikely under service conditions in many types of electrical machinery. As soon as the manufacture of phenol-formaldehyde resins became developed commercially they were employed for the manufacture of laminated pressboard. The mechanical

⁶⁶ U. S. Pat. 1,173,907, Feb. 29, 1916. Yeoll, U. S. Pat. 1,379,430-1-2-3-4, May 24, 1922, uses synthetic resins in preparing laminated printing plates.

⁶⁷ Note Novotny, U. S. Pat. 1,377,519, May 10, 1921, relating to the manufacture of printing plates from furfural resins; also 1,398,147, Nov. 22, 1921, to Novotny for producing a moldable composite body.

⁶⁸ U. S. Pat. 1,083,755, Jan. 6, 1914.

⁶⁹ J. Ind. Eng. Chem. 1, 149; Chem. Abs. 1909, 1471; 1916, 256; U. S. Pats. 1,160,362, Nov. 16, 1915; 1,213,144, Jan. 23, 1917.

⁷⁰ British Pat. 157,415, Jan. 10, 1921.

⁷¹ Raw Material 1922, 5, 97; Chem. Abs. 1922, 16, 1996.

strength of synthetic resin pressboard does not decrease with increase in temperature to an extent nearly as great as in the case of the material made from natural resins.

Phenol-formaldehyde resins have found wide use as a coating or material for impregnation of canvas or fibre. As a dielectric, dry fibre is ideal in many ways, but its tendency to absorb water affects its dielectric properties. Impregnating and binding together the fibres with a resin of course greatly reduces the tendency to water absorption. The reaction taking place in the fibre when phenol-formaldehyde resins undergo hardening develops water and the presence of this reduces the dielectric strength. It has been found more difficult and expensive to employ these synthetic resins for the manufacture of laminated pressboard and care should be taken to remove the chemically-formed water when high dielectric strength is desired. Great progress has, however, been made in the production of such pressboard and it is now being used for purposes where only the best insulators can be employed such as wireless apparatus and electric railway track insulation. Impregnated canvas is used more for mechanical than electrical purposes. It finds employment in the manufacture of noiseless gears, aeroplane propellers and in numerous other ways. The properties attainable and the preparation of laminated products are described in Chapter 24.^{70a}

Composite Cardboard or Pressboard.

Bakeland⁷¹ unites several sheets of cardboard by phenolic condensation products to form a composite cardboard or pressboard. The sheets are hot pressed to convert the binder into an infusible material. Decorative effects are obtained by making a laminated structure in various colors.⁷² Sheets of vulcanized fibre cemented by this method yield a pressboard of great strength which is much used in radio apparatus and other equipment of an electrical nature.⁷³ Superposed sheets of cloth or paper sometimes are stitched together and then saturated with a phenolic condensation product.⁷⁴ Merely sticking together sheets of paper does not give as good results as hot-pressing

^{70a} Laminated products employing a phenol-formaldehyde resin binder are prepared in a number of grades by the following companies:

<i>Company</i>	<i>Trade Name</i>	<i>Base</i>
Diamond State Fibre Co.	"Condensite Celoron"	Fibre and Canvas
Continental Fibre Co.	"Bakelite Dilecto"	Paper or Fibre
	"Continental Bakelite"	Canvas
Formica Insulation Co.	"Formica"	Paper and Canvas
Westinghouse Electric and Manufacturing Co.	"Bakelite Micarta"	Paper and Canvas

Note also Hecker and Ott, *Raw Material*, 1921, 4, 449. *Chem. Age* (New York), 1922, 495.

⁷¹ U. S. Pat. 1,019,406, Mar. 5, 1912.

⁷² Frederick, U. S. Pat. 1,284,644, Nov. 12, 1918.

⁷³ McIntosh, U. S. Pat. 1,236,460, Aug. 14, 1917.

⁷⁴ Stevenson, 1,295,230, Feb. 25, 1919.

sheets which have been thoroughly impregnated with the phenolic condensation product. Wright⁷⁵ soaks paper or cotton duck in an alcoholic solution of the resinous material, and after drying the sheets are compacted to a thick sheet or block by hot-pressing. When properly made there is very little tendency for such sheets to split along the laminated surfaces. Stevenson⁷⁶ impregnates thread or yarn with a phenolic condensation product and weaves a special fabric of any desired thickness, which is hot-pressed. Non-laminated sheets are thus obtained. The fabric also may be made and then impregnated. Taylor^{76a} produces a laminated pressboard of a composite nature from parchmented fibre.

Gears.

Conrad⁷⁷ makes a sheet stock for gears by coating cotton duck with a phenolic condensation product, hot-pressing a number of superposed sheets to make stock of the required thickness and finally baking the sheets for several hours to complete the transformation of the binder to an infusible state. During the baking operation the sheets are clamped between steel plates to prevent warping.⁷⁸ Baekeland⁷⁹ also makes gears, pulleys and other machine elements by uniting perforated metal plates or discs through the agency of a plastic mass of phenolic condensation products or of previously formed sheets made from this material and asbestos or other filler. Impregnated sheets of cotton duck, cut or punched to shape, are made into gears by Bastian⁸⁰ simply by molding together a sufficient number of these punchings, in a mold of the exact shape of the desired gear. Stevenson⁸¹ uses a mixture of cotton waste and phenolic condensation product which is molded to gear shape.

O'Connor⁸² coats one surface of paper, muslin, or other cloth with liquid Bakelite by passing between two rollers, the bottom one of which dips into a tank containing the liquid Bakelite. The fabric then is passed over a series of rollers in a steam-heated oven to dry it, after which it is cut into sheets. A plate of superposed sheets is built up by placing the uncoated side of each sheet next to the coated side of the adjacent sheet. The top and bottom sheets are placed with the coated surface inwards so as to present untreated faces on the finished

⁷⁵ U. S. Pat. 1,303,753, May 13, 1919.

⁷⁶ U. S. Pat. 1,392,535, Oct. 4, 1921.

^{76a} U. S. Pat. 1,441,133, Jan. 2, 1923.

⁷⁷ U. S. Pat. 1,167,742 and 1,167,743, Jan. 11, 1916.

⁷⁸ The Conrad Pats., No. 1,167,742 and No. 1,167,743, were held void for lack of invention, United States District Court, Southern District of Ohio, Westinghouse Electric & Manufacturing Co. vs. Formica Insulating Co., 270 Fed., 632; Chem. Met. Eng. 1921, 25, 795.

⁷⁹ U. S. Pat. 1,160,364, Nov. 16, 1915.

⁸⁰ U. S. Pat. 1,223,348, Apr. 17, 1917.

⁸¹ U. S. Pat. 1,298,816, Apr. 1, 1919; note also Grünwald, Brit. Pat. 111,664, Nov. 15, 1917, *Kunststoffe* 1922, 12, 109.

⁸² U. S. Pat. 1,284,432, Nov. 12, 1918.

plate. The layers are hot-pressed and cooled in a hydraulic press. The plate is then clamped between steel plates, to prevent warping, and is baked while being subjected to an air pressure of 140 lbs. per square inch at temperatures of 100-140° C. for about 8 hours.

Compositions containing a fibrous cellulose base are impregnated with a resinous condensation product of phenol and formaldehyde by treating the fibres with the reacting substances successively or simultaneously and causing condensation to take place within the fibres. The cellulose is usually parchmented either before or during impregnation. The usual parchmentizing agents may be employed but substances which act as catalysts in the condensation of phenol and formaldehyde are preferred. Compounds proposed for this purpose are caustic soda, ammonium or sodium zincate, stannates, stannites, antimonates, aluminates and titanates.^{82a}

Phenol-acetaldehyde resin is employed by Alexander.⁸³ Fibrous material such as cardboard or woven fabric is impregnated and coated with a condensation product of phenol or a cresol and acetaldehyde or paraldehyde. For the impregnation the product is in solution preferably in a mixture of alcohol and benzol. The material is then coated with thin films of the condensation product containing filling material, heated to set the coatings, then coated more thickly with the product containing less filling material and finally baked again. The finished material may be used in the production of sound records, printing plates, panels, matrices, etc. Several layers of fibrous material may be used to form a core united by means of the condensation product as adhesive. The preferred proportions are 100 parts of phenol to 75 parts of acetaldehyde with a mineral acid and nigrosine or zinc chloride as catalysts; or 100 parts of phenol and 35 of the aldehyde may be used and after the elimination of the acid catalyst the mass is hardened by the addition of a solution of sodium bisulphate in acetaldehyde. Composite sheet material which can be molded and used for printing surfaces, etc., is made from a fibrous body impregnated with a liquid binder capable of setting or hardening in two stages under the action of heat, such as phenol-aldehyde resinous condensation products. The body is heated to such an extent before molding that instead of remaining soft it becomes dry and crisp. The sheet is coated on both sides with a layer of the binding material containing a high proportion of a filler such as lampblack. Heat is applied until the cement is nearly hard. Coatings of cement containing a lower proportion of filler are then applied and the sheet is heated until the latter coatings are of such consistency as to be molded readily by pressure. The sheet is then molded as desired in a heated press, until the cement is completely set. The lampblack may be replaced by other fillers.^{83a}

^{82a} Metropolitan-Vickers Electrical Company, Ltd., British Pat. 169,451, 1921.

⁸³ British Pat. 176,828, 1920.

^{83a} Alexander, British Pat. 163,552, 1920.

Rods and Tubes.

A development of impregnated paper plastics is that of forming rods and tubes from the material and heating or pressing to convert the binder into an infusible, insoluble condensation product. Various processes have been devised for the purpose by Frederick.⁸⁴ The usual procedure is to impregnate paper with a phenolic condensation product and wind the paper on an expanding mandrel and causing the mandrel to expand to exert a high pressure on the inner walls of the tube. The tube then is heated to harden the binder and consolidate the convolutions into a compact tube. Kempton⁸⁵ uses an expanding mandrel which exerts a uniform internal pressure. Paper tubes which are first impregnated with sulphur and then with a phenolic condensation product are found to be substantially more water-resistant.⁸⁶

Extruded Products.

Articles such as tubes, rods or sheets are formed from a mixture of partially cured phenolic condensation product and fibrous material by heating and extruding the composition under pressure through a die. Before the pressure is released the product is cooled.⁸⁷

Composite Plates.

Plates or masses of a composite nature are constructed by Kempton⁸⁸ of sheets of asbestos impregnated with phenolic condensation product alternating with layers of wood flour molding compound. Articles such as barrier rings used in alternating current motors may be made of asbestos on the outside to resist arcing and of wood flour molding compound on the inside to afford the high dielectric qualities needed at that part of the ring. These materials are molded into a composite article by a binder of a phenolic condensation product.

An insulating material is made by Kempton⁸⁹ by placing a layer of mica or other material having high dielectric strength, between two layers of fabric impregnated with a phenolic condensation product. Frederick⁹⁰ prepares a covering for automobile running boards, floors of aeroplane bodies, etc., of superposed layers of fabric and ground cork, both impregnated with phenol-formaldehyde resin and subjected to heat and pressure.

Unusual Applications.

Among the odd or unusual applications of Bakelite, Condensite, Redmanol and other phenol-formaldehyde resinous condensation products, the following may be noted:

Curley⁹¹ renders the bows of tennis rackets warp-proof by cement-

⁸⁴ U. S. Pats. 1,284,295-6-7-8-9, Nov. 12, 1918.

⁸⁵ U. S. Pat. 1,284,363, Nov. 12, 1918.

⁸⁶ Burningham, Richter, Van Arsdell and White, U. S. Pat. 1,396,021, Nov. 8, 1921. A method of manufacturing tubes or other articles from paper impregnated with Bakelite is furnished by Bültemann, Kunststoffe, 1922, 12, 76.

⁸⁷ Egerton, U. S. Pat. 1,370,800, Mar. 8, 1921.

⁸⁸ U. S. Pats. 1,309,758, July 15, 1919, and 1,312,789, Aug. 12, 1919.

⁸⁹ U. S. Pat. 1,416,036, May 16, 1922.

⁹⁰ U. S. Pat. 1,430,541, Oct. 3, 1922.

⁹¹ U. S. Pat. 1,094,705, Apr. 28, 1914.

ing a layer of Bakelite between two strips of wood forming the bow. Golf balls have been made by Aylsworth and Smith.⁹² Tests⁹³ with propellers made of sheets of duck coated with Bakelite showed that the material possessed a number of useful properties, including elasticity, uniformity of texture, absence of warping, freedom from checking and splitting, and uniformity of all propellers made from the same mold, besides being moisture-proof and oil-proof. The propellers were made by pressing together 5 or 6 coated sheets to form a board, which was then shaped with a saw and finally molded under pressure at 350° F.⁹⁴

Ball⁹⁵ has made use of these resinous compounds for violin bows. In preparing a filling for teeth, Albrecht⁹⁶ uses a solution of a phenol in formaldehyde diluted with a viscous retarding agent (glycerol), and mixed with a condensing agent, to obtain a preparation which will readily penetrate into the smallest cavities in the teeth, and slowly harden there, at the temperature of the body. A material for dental and other purposes is prepared by condensing phenol with trioxymethylene, using an alkaline catalyst, to yield an initial resinous condensation product. The mixture is finally hardened by means of an aqueous solution of an acid such as sulphuric, hydrochloric or particularly phosphoric acid or by a mixture of fuming sulphuric acid with glacial acetic acid. Phosphorus pentoxide may be employed as a catalyst and as a drying agent. Sodium bisulphite may be used to prevent oxidation. By spinning raw viscose with phenol-aldehyde resin in a bisulphite bath Bronnert⁹⁷ has produced a modified form of viscose silk.

Sweetland, Manning and Hilpert⁹⁸ prepare a filter cloth resistant to the corrosive action of fatty acids by applying to a woven metallic fabric, so that the interstices are only partially closed, a thin coating of a composition containing a phenol condensation product which is inert to fatty acids.

Another unusual application is in the production of blocks containing orifices to be used in the extrusion of artificial silk solutions. A series of parallel wires are arranged in a mold and surrounded by a phenol-formaldehyde resinous condensation product. This material is then hardened and the block is cut into plates transverse to the wires. The latter are dissolved by treatment with acids affording a plate containing fine orifices which can be used in forming artificial silk fibres.⁹⁹

Phenol-aldehyde condensation products are used by Froom¹⁰⁰ in connection with the manufacture of soles and heels for shoes.

⁹² U. S. Pat. 1,134,433, Apr. 6, 1915.

⁹³ J. S. C. I. 1920, 338R.

⁹⁴ Note also Nilson, U. S. Pat. 1,308,527, July 1, 1919.

⁹⁵ German Pat. 254,750, June 9, 1912.

⁹⁶ J. S. C. I. 1917, 91; U. S. Pat. 1,205,957.

⁹⁷ U. S. Pat. 1,374,718, April 12, 1921.

⁹⁸ J. S. C. I. 1919, 276A; U. S. Patent 1,292,535.

⁹⁹ Schülke and Elsner, British Pat. 161,526, 1922; *Kunststoffe* 1922, 18, 142.

¹⁰⁰ British Pat. 176,404, Sept. 7, 1920. Absorptive material by carbonizing a condensation product of resorcin and formaldehyde, see Wallerstein, U. S. Pat. 1,442,372, Jan. 16, 1923.

Clutch Facing and Brake Lining.

A disc clutch facing is made by Achtmeyer¹⁰¹ from asbestos and phenol-formaldehyde resin prepared with the aid of sodium tungstate as a catalyst. The composition is hardened by baking. Achtmeyer¹⁰² impregnates brake linings with a resin prepared from phenol and methylene diphenyl diamine. The impregnating composition also contains a small proportion of paraform. The impregnated lining is baked at a temperature gradually increasing to 400° C. Fibrous compositions for the manufacture of brake blocks, discs for friction drives, or stair treads are obtained by treating one or more layers of asbestos mill-board with a phenol-formaldehyde resinous condensation product.^{102a}

A clutch facing is made by Fisher^{102b} by impregnating asbestos board rings with a solution in alcohol of rosin and a soluble resinous phenol-formaldehyde condensation product.

Abrasive.

Polishing or abrasive compositions are prepared according to Baekeland¹⁰³ by incorporating an abrasive material with a phenolic substance and formaldehyde and transforming the mixture into an insoluble product by the application of heat and pressure.¹⁰⁴

Bearings and Treads.

These resins also have been found valuable in self-lubricating bearings by Baekeland.¹⁰⁵ To the resin he adds graphite and also asbestos or wood pulp to give strength to the composition. Molded articles adapted for use as pulleys are formed with a main body portion made up of cotton or other fibre impregnated with phenol-formaldehyde condensation product and an insert of similar material containing a lubricant, e.g., graphite.^{105a} Hopp¹⁰⁶ combines this type of synthetic resin with an abrasive material (carborundum) and applies the mix to a base of metal, rubber, or textile material to make safety-treads.

Roofing.

The relative cheapness of the pitches used in roofing does not leave much of a field for roofing made from phenol-formaldehyde condensation products. Aylsworth¹⁰⁷ has made use of chlor naphthalene in conjunction with such synthetic material. Roofing of this character

¹⁰¹ U. S. Pat. 1,429,266, Sept. 19, 1922.

¹⁰² U. S. Pat. 1,429,267, Sept. 19, 1922.

^{102a} Frood, British Pat. 166,916; J. S. C. I. 1921, 40 655A.

^{102b} U. S. Pat. 1,436,158, Nov. 21, 1922.

¹⁰³ J. S. C. I. 1910, 99; U. S. Pat. 942,808, Dec. 7, 1909.

¹⁰⁴ Note also Aylsworth, U. S. Pat. 1,090,440, Mar. 17, 1914.

¹⁰⁵ U. S. Pat. 1,054,265, Feb. 25, 1913.

^{105a} Kempton, U. S. Pat. 1,392,173-4, Sept. 27, 1922.

¹⁰⁶ U. S. Pat. 1,156,081, Oct. 12, 1915.

¹⁰⁷ U. S. Pat. 1,077,113, Oct. 28, 1913.

possesses a high degree of non-inflammability. Chlor naphthalene (mono, dichlor or higher chlor compounds) is incorporated with the synthetic resin to the extent of 10-60 per cent of the latter. One or two parts of asbestos are added to 2 parts of this mixture and the composition is sheeted on calender rolls. The sheets may be pressed in dies, in imitation of tiling.

Gaskets.

Packing material or gaskets are made by Baekeland¹⁰⁸ from asbestos felt impregnated with a phenol-formaldehyde condensation product. Metal reinforcing material may be present and the addition of graphite or talc to prevent sticking is recommended. The addition of an oleic or other fatty acid is proposed by Chappell.¹⁰⁹ He heats for 2-6 hours, at 100-200° C., a mixture containing phenol, 100 parts, formaldehyde, 60-120 parts, oleic acid, 20-60 parts, and ammonium oleate, 1-15 parts, as a condensing agent. An oleic acid-formaldehyde compound is supposed to be formed and to react with the phenol condensation product (saligeno-saligenin).

Waxed Paper.

Gesell¹¹⁰ treats paper with a mixture of a wax (paraffin or ceresin) and a soluble phenolic condensation product. The coating or impregnating mixture is dissolved in a common solvent. The paper is heated to change the soluble condensation product into the ultimate insoluble and infusible form. The finished coating possesses a considerable degree of flexibility due to the effect of the wax.

Paper Sizing.

Baekeland¹¹¹ treats wet paper pulp with an alkaline solution of a phenolic condensation product and precipitates the latter on the pulp by the addition of acid or a salt which brings about precipitation. For sizing paper, alkaline solutions have been proposed, which contain condensation products of aldehydes with phenols or hydroxynaphthalene compounds and small amounts of alkali sulphites or other suitable materials which prevent the absorption of oxygen by the resin solution. Generally an addition of 0.5 per cent of sodium sulphite is sufficient to prevent coloration of the alkaline resin solutions by the oxygen of the air and permit the production of a well-sized white paper.¹¹²

Alkali Salts.

Water-soluble alkali salts of phenol-formaldehyde resins are dissolved in less than the equivalent amount of alkali and are salted out

¹⁰⁸ U. S. Pat. 941,605, Nov. 30, 1909.

¹⁰⁹ U. S. Pat. 1,102,473.

¹¹⁰ U. S. Pat. 1,277,904, Sept. 3, 1918.

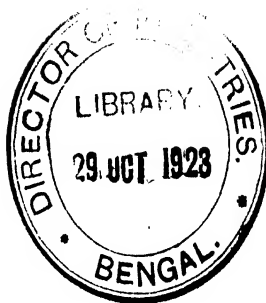
¹¹¹ U. S. Pat. 1,160,365, Nov. 16, 1915.

¹¹² Holzverkohlungs-Ind. A.-G. German Pats. 338,395; 339,594 and 342,255, J. S. C. I. 1921, 40, 766A, 1922, 41, 95A.

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of solution. When using an equivalent or greater quantities of alkali the material cannot be salted out. The substances obtained are soluble in water but the solutions are decomposed by carbon dioxide or on heating with partial precipitation of the condensation product. The product is said to find application in the textile industry.¹¹³

¹¹³ Bucherer, German Pat. 350,043, 1918; J. S. C. I. 1922, 41, 728A.



Chapter 10.

Aldehydes.

The present chapter briefly discusses a number of amorphous or resinous products obtained from aldehydic bodies by self- or inter-condensation. Among these the acetaldehyde and aldol resins offer a field for more extensive investigation. To the resin synthesist the directions for making aldol by numerous processes are of interest as the problem in these investigations has been how to prevent resinification. The commercial derivation of acetaldehyde from acetylene has revived interest in aldehyde resin, long ago investigated by Döbereiner and Liebig. The author has observed the formation of a species of aldehyde resin by passing air or oxygen, free from carbon dioxide, through alcoholic potash containing a catalyst. Substances, earlier described as *polymers*, later frequently are designated *resinous*. The interesting acrolein polymers studied by McLeod become, at least in some modifications, the acrolein resins of Moureu. Aldehydes of the aromatic or cyclic series probably offer greater promise of yielding resins having the qualities desired commercially. Resinification of aldehydes generally represents a high degree of polymerization or condensation or of these processes combined. This appears a necessary step in the building-up of a complex devoid of crystalline properties, having the appearance and fracture recognized as resinous. Other things being equal, the greater the molecular weight of the parent substance, the greater the likelihood of obtaining resinous products of the resistant qualities demanded in the industry.

The Resinification of Acetaldehyde.

Döbereiner¹ observed that a solution of alcoholic potash when warmed with aldehyde separated a yellowish or brown resin-like body. Liebig² noted that an aqueous solution of aldehyde, warmed with caustic potash, immediately became yellowish and turbid and quickly there separated a reddish brown substance which could be drawn out into long threads. Liebig named this product aldehyde resin although he did not regard the name *resin* entirely applicable. The resin forms by the action of caustic potash on alcohol, especially quickly in the presence of air. It also forms from acetal. The distillate from

¹ Annalen d. Pharm. 14, 133.

² Ibid. 140.

alcohol, manganese dioxide and sulphuric acid, when made alkaline with caustic potash, heated and then diluted with water, yields a dark brown mass which forms lumps in hot water. On cooling a hard product is obtained which may be pulverized to a light brown powder. The product is, however, somewhat soluble in water. When dried at room temperature and subsequently over a water bath the resin was reported by Liebig to ignite spontaneously. If precipitated from aqueous alkaline solution by dilute sulphuric acid, the resin is not soluble in water. Resin obtained in this way was dissolved in alcohol, water added and the alcohol boiled off.

The alkali employed for resinification is used up to a slight extent in the formation of organic acid salts.³ The penetrating odor of the resin noted by Liebig is due to a volatile oil which clings tenaciously to the resin, according to Weidenbusch.⁴ The oil is oxidized by air to a resinous body. Aldehyde resin is described by Weidenbusch as a bright orange yellow powder, becoming lighter in color on long drying at 100° C. It is soluble in alcohol and ether and slightly soluble in water. Alkalies scarcely affect it. No spontaneous ignition such as was reported by Liebig was noted by Weidenbusch. The alkaline liquors were found to contain formate.

Ekecrantz Process.

The preparation of resin from acetaldehyde has been carried out by Ekecrantz⁵ as follows: a mixture of acetaldehyde and alcohol is prepared and cooled to -20° C. A 10 per cent alcoholic solution of caustic soda is added at a temperature below +10° C. After keeping cold for some time the mixture is brought to room temperature and is allowed to stand for 24 hours, then is heated under a reflux condenser until the aldehyde odor has disappeared. Alcohol is removed by distilling under reduced atmospheric pressure, the temperature not exceeding 30° C. A thick reddish brown residue is obtained. It is treated repeatedly with hot 5 per cent caustic soda solution. The mass sets on cooling to a brittle resin. Purification may be had by dissolving the resin in glacial acetic acid and precipitating with water. A voluminous yellowish brown precipitate is obtained. The acid portion of the aldehyde resin which is in solution associated with the caustic soda is separated as follows: first warm the alkaline solution, then cool and filter. Hydrochloric acid is added to exactly neutralize the alkali. On extraction with ether and evaporation a yellowish brown viscous residue appears. Purified aldehyde resin is a yellowish brown hygroscopic powder, soluble in chloroform, alcohol and acetone but only partly soluble in benzol and ether. It is insoluble in water and in petroleum ether. At 105° C. the resin sinters and at 130-140° C. it melts and

³Liebig, *Ibid.* 158.

⁴*Annalen d. Chem.* 66, 153.

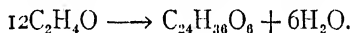
⁵*Arkiv för Kemi* 4, No. 27, 1; *Chem. Centralblatt* 1912, II, 1194; *Böttler, Kunstharzen*, 1919, 42.

intumesces. No technical application of this aldehyde resin is thus far known according to Bottler.⁶

Elementary analyses of acetaldehyde resin by various observers follow. Ekecrantz ascribes the variation in analytical results to a fluctuating water content.

	<i>Liebig</i>	<i>Weidenbusch</i>	<i>Ekecrantz</i>
Carbon	73.34	76.40	70.07
Hydrogen	7.76	7.97	7.83
Oxygen	18.90	21.63	22.1

Ekecrantz was able, by means of solvents, to separate aldehyde resin into two components, α and β resin, each represented by the formula $C_{24}H_{38}O_6$ and supposedly obtained by the reaction



The alpha resin dissolves easily in benzol but the beta resin is only slightly soluble in this solvent.

Hammarsten's Investigations.

Hammarsten⁷ has studied the constitution of aldehyde resins from acetaldehyde. He allowed aqueous solutions of acetaldehyde to remain for 5 to 6 days with an equal volume of aqueous potassium hydroxide solution (10 per cent) at ordinary temperatures. The solution was exactly neutralized with hydrochloric acid, whereby the ordinary red resin was precipitated. Further addition of a large volume of concentrated hydrochloric acid to the filtrate causes the separation of a very pale straw-yellow resin, which has a melting point 120-130° after softening at 105° C., and commences to decompose above 200° C. This resin appears to be a definite substance containing 66.13-66.73 per cent carbon and 7.45 to 7.68 per cent hydrogen with a molecular weight of 396-412. The yellow resin may be first formed since aldehyde solutions are initially colored yellow by alkali and then clouded by the formation of a yellow precipitate, which darkens in color as it increases in amount. Hammarsten is uncertain whether the red resin is formed independently or through the yellow variety. An alkaline solution of the yellow resin does not become turbid when preserved which suggests the probability that the red resin forms through a different course of the reactions leading to resinification. The formation of aldehyde resin is not to be regarded as the final stage in the condensation of acetaldehyde. In solutions of the latter, the formation of acetate, ethyl alcohol, aldols, yellow and red resin, proceeds simultaneously.⁸

Improving Stability.

The stability of aldehyde resins toward water is improved by dissolving the resin in an organic solvent and precipitating by water. Resin prepared by treating acetaldehyde with caustic alkali is dissolved in glacial acetic acid and precipitated by water. The resin may be heated to harden it. Crotonaldehyde, similarly treated with caustic alkali, forms a viscous liquid. This is dissolved in acetone and precipitated by water. Resins obtained by this procedure are

⁶ Kunsthazzen, 1919, 42.

⁷ Annalen, 1920, 421, 293; J. Chem. Soc. 1920, 117-118, i. 818; Chem. Abs. 1921, 507.

⁸ By-product resins of a ketonoid or aldehydic nature are obtained by the action of alkali on pyroligneous acid. See process of Chute described in Chapter 14.

soluble in alcohol, acetone, benzol, trichlorethylene, linseed oil, etc.⁹ Resins yielded by the condensation or polymerization of aldehydes (such as acetaldehyde resins obtained by the action of alkali) are rendered more stable toward water by grinding in a ball mill with acetic acid of 3 per cent strength. The product may be dissolved in fatty oil, alcohol or volatile hydrocarbons and used in the manufacture of varnish.¹⁰

Resins obtained from aliphatic aldehydes are subjected to oxidation either in the molten state or dissolved or suspended in a liquid, yielding products which are soluble in aqueous solutions of borax and soda. The resin may be dissolved in glacial acetic acid and treated with ozonized oxygen, or with oxygen in the presence of manganese acetate. Water is added to precipitate the product. Alternatively, the resin is suspended in water containing potassium permanganate, and oxygen is passed through to oxidize it. The products may be hardened by heating and may be used in manufacturing oil varnishes.¹¹

Aldehyde Derivatives.

The dichlor aldehyde, $C_2H_2Cl_2O$, assumes a dense form which finally becomes a white amorphous mass with an outward semblance of porcelain. On heating to $120^\circ C$. it is reconverted to a liquid.¹² A mercury compound of the formula $C_2H_2O.NHg_2$ is formed by adding to a solution of mercuric nitrate acidulated with nitric acid either acetylene or an alcoholic solution of aldehyde. By warming this mercury compound with caustic soda or potassium cyanide solution much aldehyde resin is formed.¹³ Aldehyde dissolves cyanamide and in 24 hours changes into a resinous body insoluble in water but soluble in alcohol.¹⁴ Cyanamide reacts violently with chloral¹⁵ forming a sticky resin which hardens on exposure to air. It is moderately soluble in alcohol, ether and chloroform. The substance turns brown and decomposes on heating to $210^\circ C$.

Aldehyde Gum.

Acetaldehyde is digested with an aqueous solution of barium hydrate, and the barium precipitated as the carbonate by carbon dioxide. After filtration to remove barium carbonate and aldehyde resin, the solution is evaporated and a gummy syrup is obtained.¹⁶

Base Having the Formula $C_{10}H_{12}N_2O_8$.

By heating dialdan ($C_8H_{14}O_8$) with aqueous ammonia in a tube to $100^\circ C$., then evaporating the ammonia, a resinous mass is obtained which is crystallized from ether and yields plates which are easily soluble in water, alcohol and ether. The aqueous solution separates an amorphous body on standing.¹⁷

Sebacic Dialdehyde.

Decanedial, $C_{18}H_{36}(CHO)_2$, is a colorless, oily liquid with a pleasant odor, which polymerizes rapidly to a vitreous form if not taken up in a solvent or fractionated at once.¹⁸ The distillate likewise changes in about one hour to the glassy modification. It darkens superficially on standing and is insoluble in ordinary solvents. The glassy form very slowly gives the typical aldehyde reactions. Boiling dilute sulphuric acid gradually depolymerizes it.

⁹ Consortium f. Elektrochem. Ind. Ges.; Chem. Age, London, 1922, 7, 355; British Pat. 182,459, 1922.

¹⁰ Consortium für Elektrochemische Industrie Ges., Chem. Age, London, 1922, 7, 538. British Pat. 184,442, 1922; Chem. Abs. 1923, 218.

¹¹ Consortium für Elektrochemische Industrie Ges., The Chemical Age (London), 1922, VII, 612. British Pat. 185,107, 1922; Chem. Abs. 1923, 218.

¹² Chem. Age, London, 1922, 7, 78.

¹³ Hofmann, Ber. 31, 2213, 2784.

¹⁴ Knop, Annalen 131, 253.

¹⁵ Schiff, Fileti, Berichte 10, 426.

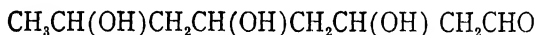
¹⁶ Tollens, Ber. 17, 660.

¹⁷ Wurtz, Jahresbericht 1880, 524.

¹⁸ Rosenmund, Zetzsche, and Enderlin Ber., 1922, 55B, 609.

Aldol Formation.

One of the drawbacks in aldol condensations, according to Kyriakides,¹⁹ is the fact that the aldehydes and aldols are usually very sensitive towards the alkalis, so that there is more or less resinification during the reaction. The older experimenters avoided this trouble, partially, by using weak alkaline compounds to effect the condensation; while of late the tendency has been to use strong alkalis in presence of inert organic solvents, which latter extracted continually the sensitive compounds from the sphere of action of the alkali.²⁰ It is noted by many that, in carrying out these condensations, the end of the reaction is judged by the appearance of a light yellow color in the aldol liquid. This color is a sign of the formation of higher condensation products and resins. For a good aldol formation it is necessary that the liquid should be perfectly colorless. Aldol condensation is the principal reaction in the action of dilute alkali upon acetaldehyde. Hammarsten²¹ observes that aldol does not disappear during the later reactions such as resin formation, even at higher temperature and longer reaction times. The first condensation product is acetaldol, but this is changed in part to higher aldols, of which



has been isolated. In no experiment, under the conditions reported, was less than 40 per cent of aldol obtained from 0.5 N acetaldehyde solution. This may be taken to indicate that the higher molecular aldols do not form aldehyde resins. Acetaldol, however, does give rise to resins. Cannizzaro's reaction proceeds much slower with acetaldehyde than the aldol formation; in no case, even with the greatest variation in temperature, times of reaction, concentration, and condensation agents, did more than 12 per cent of the acetaldehyde react according to this reaction. With the higher concentrations of alkali the reaction was more pronounced, in relation to the aldol condensation, than with the lower concentrations, at least when potassium hydroxide was the condensing agent. With barium hydroxide the concentration was not so important. Lead hydroxide had a specific action, since a noticeable aldol condensation resulted but neither the Cannizzaro reaction nor resin formation. The aldehyde resin consisted of at least two constituents of different composition, the ordinary red aldehyde resin, investigated by Ekecrantz, and separable into α - and β -resins, and a light yellow, alkali-soluble resin.

Condensation by Acids.

Hydrochloric acid brings about the formation of a resin from acetaldehyde. This resin was observed by Wurtz²² when preparing aldol.

¹⁹ J. Am. Chem. Soc. 1914, 36, 532.

²⁰ See Hibbert, U. S. Pat. 1,086,048, Feb. 3, 1914.

²¹ Ann. 1920, 421, 293.

²² Wurtz, Dict. de chimie, Supplement Vol. I, 87; Rev. gén. chim. 1907, 10, 51.

When made in the cold the resin is of a yellow color. Prolonged action of the acid yields a darker resin. Glassy solids have been obtained from aldol by warming with hydrochloric acid.

A method of making technical aldehyde resin is to subject an aldehyde to the action of a warm mineral acid or a salt of an acid nature.^{22a} Thus acetaldehyde may be converted into a resin by first heating to 40° C. with sulphuric acid and then raising the temperature to 100° C. until a sample sets on cooling. The product is then raised to 150° C. for a considerable period of time and this exposure to heat brings about conversion to a hard resin. Sodium bisulphate may be used in place of sulphuric acid. Crotonaldehyde also may be resinified in a similar manner. Resins made in this manner have low melting points and the suggestion has been made that they be added to other resins of higher melting point to render the latter more fusible. A further hardening may be brought about by fusion with a metal oxide or by esterifying with glycerol.

In order to avoid polymerization brought about by contact of aldol with the agent of condensation Grignard and Rief²³ employ a large amount of ether to remove the product as fast as formed. A saturated aqueous solution of sodium sulphite is preferred as the condensing agent.

Aldol forms a complex with "dimedon" (dimethyldihydroresorcinol) which can be differentiated from the analogous acetaldehyde complex by its insolubility in light petroleum.²⁴

According to Grunstein²⁵ aldol condensation may be effected by a smooth and easily controlled reaction without the addition of ice or an organic solvent, if the acetic acid contained in the aldehyde is first neutralized with the requisite quantity of sodium hydroxide solution, and a catalyst of alkaline reaction is then gradually introduced with cooling. As a catalyst aqueous alkali hydroxide, not exceeding in quantity 1 part of alkali to 100 parts of acetaldehyde, may be employed, or equally favorable results are obtained with alkali or alkaline-earth carbides and cyanides, or alkaline-earth hydroxide. In all cases the presence of a small quantity of water appears to be essential. To prevent the condensation proceeding too far, with formation of resins, etc., it is stopped before all the acetaldehyde has been converted into aldol by adding sufficient hydrochloric or acetic acid to neutralize the alkali, separating the salt, and distilling the products in vacuo.²⁶

Aldol Ammonia ($C_4H_8O_2.NH_3$).

This compound was prepared by Wurtz²⁷ who conducted ammonia gas into a solution of aldol in ether. The product is a water-soluble syrup which becomes resinous when dried in a vacuum.

Crotonaldehyde ($CH_3.CH:CH.CHO$).

Treatment with sodium amalgam or zinc and hydrochloric acid causes crotonaldehyde to become resinified.²⁸ In the preparation of crotonaldehyde by reacting on acetaldehyde with sodium sulphite, care has to be taken to carry out the reaction in the cold to prevent the formation of aldehyde resin.²⁹ A viscous resin may be formed by treating crotonaldehyde with caustic alkali. The mass is dissolved in acetone and precipitated by adding water. The precipitated resin

^{22a} Consortium für Elektrochemische Industrie Ges., Chemical Age, London, 1922, 7, 943; British Pat. 187,619, 1922.

²³ Bull. Soc. Chim. (4), 1, 114-117; Chem. Abs. 1907, 1, 1389.

²⁴ Fricke Z. physiol. Chem., 1921, 116, 129; J. S. C. I. 1922, 41, 268A.

²⁵ British Pat. 147,119, July 7, 1920; J. S. C. I. 1922, 41, 78A.

²⁶ See also Grunstein, British Pat. 101,636, Sept. 27, 1916.

²⁷ Jahresbericht 1873, 474; Beilstein 3rd Ed., Vol. 1, 964.

²⁸ Beilstein, 3rd Ed., 1, 959.

²⁹ Seyewetz and Bardin, Compt. rend. 141, 259, 1905.

is then hardened by heating it alone or dissolved in linseed oil.³⁰ Tricrotonylene amine, $C_{17}H_{24}N_4 + 6 H_2O$, is obtained by heating aldol or crotonaldehyde with ammonia. On heating the amine with hydrochloric acid, a resin is formed together with ammonium chloride.³¹ Crotonaldehyde phenylhydrazone, $C_{10}H_{12}N_2$, is decomposed by glacial acetic acid into a resin and acetylphenylhydrazine. With hydrochloric acid the phenylhydrazone is hydrolyzed partly to a resin.³²

β Di Isobutylene Aldehyde.

This product is formed by passing dry hydrochloric acid into isobutyraldehyde.³³ It is a heavy bodied oil which resinifies on heating with alkalis.

Capronaldehyde.

With cold concentrated caustic soda solution δ -hydroxycapronaldehyde yields a white crystalline precipitate quickly changing on standing or gently warming into a dark resinous product. Ammonia does not cause this change. With phloroglucinol and concentrated hydrochloric acid a white amorphous precipitate is obtained.^{33a}

Acrolein. ($CH_2:CH.CHO$).

On keeping, acrolein changes readily into a white amorphous product (disacryl) which is not soluble in water, acids, alkalis or alcohol.³⁴ A soluble form known as acrolein resin is prepared by heating acrolein with 2 to 4 volumes of water at $100^\circ C$. for several days. A brown resin is formed which begins to melt at $60^\circ C$.³⁵ The product is somewhat soluble in water and is easily soluble in alcohol or ether.

Polymerization is greatly accelerated in the presence of alkaline substances. The temperature and time of treatment affect the character of the resulting polymer. This explains results which otherwise would appear conflicting.

Hexacrol acid, $C_{18}H_{24}O_6$. Aqueous or alcoholic potash reacts with acrolein to form a yellow amorphous substance, insoluble in water but easily soluble in alkalis, alcohol or ether. Silver oxide yields the same product.³⁶ Acrolein reacts with ammonia forming a red amorphous substance soluble in alcohol, ether, water and acids.

In sealed tubes exposed to diffuse daylight acrolein is unchanged after 2 months; winter sunlight solidifies about $1/3$ in 12 days; in a quartz tube radiation from a mercury vapor lamp solidifies it in 1.5 hours. Temperatures over 60° cause more or less polymerization in 12 hours.³⁷

³⁰ Consortium f. Elek. Ind. Ges.; Chem. Met. Eng. 1922, 27, 1042.

³¹ Wurtz, Bull. soc. chim. 34, 486.

³² Wegscheider and Spath. Monatsh., 31, 997.

³³ Oekonomides, Bull. soc. chim. 36, 209.

^{33a} Helferich and Malkomes, Ber. 1922, 702; Chem. Abs. 1922, 3065.

³⁴ Redtenbacher Annalen 47, 141, Beilstein, 4th Ed., Vol. 1, 726.

³⁵ Geuther, Cartmell, Annalen 112, 10; Beilstein, 3rd Ed., Vol. 1, 958.

³⁶ Claus, Annalen, Spl. 2, 120.

³⁷ Moureu, Murat and Tampier, Ann. chim. 1921, 15, 221; Compt. rend. 1921, 172, 1267.

McLeod's Investigations.

All alkalis, both mild and caustic, were found by McLeod³⁸ to transform acrolein in cold aqueous solution quantitatively into amorphous polymeric substances. Only traces of alkalis are required and the transformation takes place with marked evolution of heat.³⁹ The polymer is insoluble in aqueous sodium carbonate solution but forms a red colored solution in 10 per cent aqueous sodium hydroxide. Digesting in this solution for a short time at 100° C. and then neutralizing with hydrochloric acid precipitates an amorphous substance of very high melting point. Its weight is about one half that of the polymer put into solution. Some experiments carried out by McLeod on acrolein polymers are instructive. 23.5 gms. acrolein dissolved in 184 cc. cold water, treated with 0.1 gm. potassium carbonate dissolved in 2 gms. water caused immediate turbidity and soon a voluminous white substance separated. After 18 hours the odor of acrolein had disappeared. An additional quantity 0.1 gm. of the carbonate was added and after standing for 24 hours longer the precipitate of polymeric acrolein was found to weigh 22.5 gms. The product proved to be insoluble in hot water, carbon disulphide, benzol, ether, petroleum ether and glacial acetic acid, but dissolved readily in warm 95 per cent alcohol. A strong odor of acrolein was observed on warming the polymer with dilute acids or alkalis or on heating alone to 100° C. The substance softened at 83° C. and decomposed with gas evolution at 94-95° C. The polymeric compound obtained by Nef, mentioned above, softens at 115° C. and decomposes at 128-130° C. In 10 per cent sodium hydroxide solution Nef's polymer dissolves and on heating gives the same end product as that obtained by McLeod. Neither polymer could be obtained in a crystalline form. When heated in a distilling flask placed in a bath reaching a maximum temperature of 220° C. much tar formed and about 20 per cent of acrolein was recovered.

Insoluble Polymer.

The polymer obtained by heating the initial polymer in sodium hydroxide solution is insoluble in all the usual organic solvents and does not melt when heated to 180° C.

Hydracrylic Aldehyde.

The same final product is obtained with hydracrylic aldehyde and sodium hydroxide, although in this case McLeod did not find any insoluble polymer to be deposited from alkaline solutions on standing in the cold.

³⁸ Am. Chem. J. 1907, 20, 37.

³⁹ Nef obtained a polymer from acrolein and barium hydrate. Ann. Chem. 335, 220.

Restricted Polymerization.

Moureu and Dufraisse⁴⁰ find that polymers or resins of better solubility than that prepared by McLeod can be obtained by limiting the polymerization of acrolein. Their procedure is to dissolve pure acrolein⁴¹ in water and to add 1 per cent of a resinifying agent. A voluminous white precipitate forms and is immediately filtered, washed and dried *in vacuo*. A white powder is obtained, insoluble in water and hydrocarbons but very soluble in the cold in many organic solvents, particularly alcohols, ketones and acids. These solutions may be used as varnishes. The resin in powdered form agglomerates to a viscous mass at temperatures between 80 and 110° C.

Reagents which bring about the polymerization of acrolein to a resin are alkali carbonates, potash, soda, lime, lead hydroxide, ammonia, methylamine, aniline, ferric chloride and lead acetate. Free mineral acids are unsuitable. The reaction takes place rapidly in the cold. Concerning resins prepared by the reaction of acrolein on phenols see Moureu, Chap. 8.

Glyoxal (oxalaldehyde) $\text{ClHO} \cdot \text{CHO}$ in aqueous solution, evaporated on the water bath, affords a water-containing amorphous transparent form of this substance which is very soluble in water. On drying in a vacuum at 110-120° C. the product is only very slightly soluble in water. It polymerizes easily.⁴² Dichloral Methylene Glycolate ($\text{C}_2\text{H}_2\text{O}_4\text{Cl}_2 = \text{CCl}_2 \cdot \text{CHOH} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CHOH} \cdot \text{CCl}_2$) is obtained by the condensation of chloral with formaldehyde in the presence of concentrated sulphuric acid. It is a resinous body which is stable in the presence of warm concentrated sulphuric acid.⁴³

Benzaldehyde.

Ciamician and Silber⁴⁴ studied the action of light on benzaldehyde and other aldehydes and observed in many cases the formation of resin. When benzaldehyde was exposed to sunlight for a protracted period a yellow, hard, resinous body was obtained which on solution in benzol and precipitation by petroleum ether was purified to a white, resinous powder softening at 100-101° C. This exhibited the same composition as hydrobenzoin but its molecular weight was four times greater. When benzaldehyde was exposed in alcoholic solution resin also was formed. This reaction was further examined by Ciamician and Silber.⁴⁵ 35 grams benzaldehyde was exposed to light for an entire summer. A thick, yellowish brown mass was obtained which on distillation with steam to remove unchanged benzaldehyde yielded 26 grams of a solid, brittle, resinous mass. This was dissolved in ether, washed with sodium carbonate solution, evaporated to dryness and the residue dissolved in

⁴⁰ British Pat. 141,058, 1920; J. S. C. I. 1921, 40, 858A. Regarding stabilization of acrolein by means of phenol see Moureu, U. S. Pat. 1,436,047, Nov. 21, 1922.

⁴¹ Made according to process described in Comptes rend. 169, 621.

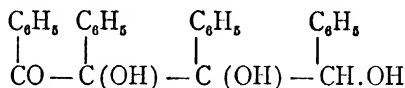
⁴² Beilstein, 3rd Ed., 1, 965.

⁴³ Pinner, Ber. 31, 1936.

⁴⁴ Ber. 1901, 34, 1538.

⁴⁵ Ber. 1903, 36, 1575.

benzol. The addition of petroleum ether precipitated a white pulverulent substance melting at 125-130° C. and which had the same elementary composition as benzaldehyde. In benzol the molecular weight was found to be represented by the formula $(C_7H_6O)_9$. Hence the resin appears to be a simple polymerization product. The resin obtained by exposure of benzaldehyde in alcohol solution had a different composition corresponding to the formula $4C_{14}H_{14}O_2$. Molecular weight determinations in glacial acetic acid^{45a} gave the value $4C_7H_6O$. The observation was made by Ciamician and Silber that the condensation product united with phenylhydrazine and semicarbazide. An investigation of these compounds suggested the possibility that the condensation product was of a ketonic nature and the following formula was suggested:⁴⁶



Other Aromatic Aldehydes.

Ciamician and Silber⁴⁷ found anisaldehyde to become partially resinified on exposure to light. Benzoin also yielded a resinous mass. Benzoin and benzaldehyde exposed to light yielded some resinous material.⁴⁸ Benzophenone and formic acid also yielded a small amount of resin on exposure to light. Benzil dissolved in ethyl alcohol on exposure to light likewise yielded a resin.

Cinnamic Aldehyde.

Formaldehyde reacts with cinnamic aldehyde, in the presence of calcium or barium hydrate, at temperatures above 50° C. to form a resin.⁴⁹ In studying the reaction between benzaldehyde, safrol and isosafrol under the influence of light Ciamician and Silber⁵⁰ obtained resinous products. That from benzaldehyde and safrol melted between 150-180° C., and from benzaldehyde and isosafrol, between 170-180° C. Tetrachlorbenzaldehyde, treated with chlorine at 100-130° C. in the presence of light, particularly of ultraviolet rays, is converted into tetrachlorobenzylidene chloride.

Phenyl Acetaldehyde, $(C_6H_5.CH_2.CHO)$

This compound polymerizes very readily to form a soft sticky resin having unpleasant odor. The tendency to spontaneous conversion to a resinous substance is so pronounced that the compound cannot be kept for more than a day without being diluted by some solvent. Phenyl acetaldehyde is easily resinified by acids.⁵¹ The formation of aldehydo-acids by the action of chloroform and sodium hydroxide on salicylic acid (Tiemann and Reimer reaction) is accompanied by the production of some resinous matter.⁵² Salicylic aldehyde forms a resinous substance when warmed with acetyl benzoyl $(ClH_3.CO.CO.C_6H_5)$

^{45a} Ber. 1909, 42, 1387.

⁴⁶ Benzaldehyde at 200° gives toluene and methylcyclohexane (Ipatief, J. Russ. Phys. Chem. Soc. 1906, 38, 75); at 280°, toluene, dibenzyl and resinous products are obtained.

⁴⁷ Ber. 1901, 34, 1539.

⁴⁸ Ber. 1903, 36, 1578.

⁴⁹ Van Marle and Tollens, Ber. 1903, 36, 1347.

⁵⁰ Ber. 1909, 42, 1391.

⁵¹ Rosenmund and Zetzsche, Ber. 1921, 54B, 425; Chem. Abs. 1921, 2436.

⁵² Wayne and Cohen, J. Chem. Soc. Trans. 1922, 1022.

and aniline with alcohol as a solvent medium.¹³ In preparing protocatchu-aldehyde from pyrocatechine, chloroform and caustic soda a black resin is formed.¹⁴ The preparation of tetrahydronaphthalene aldehyde is accompanied by much resinification.¹⁵

¹³ Borsche and Titsingh, Ber. 1909, 42, 4283.

¹⁴ Tiemann and Koppe, Ber. 14, 2015, 1881.

¹⁵ Weil and Ostermeier, Ber. 1921, 54B, 3271.

Chapter II.

Furfural Resins.

Furfural (Furof, Furfuraldehyde, $C_4H_3O \cdot CHO$) is readily prepared from pentosan or pentose-containing substances by digestion with diluted hydrochloric or sulphuric acids. Thus, materials such as bran, oat-hulls and corn cobs serve as a source of the raw material. In France, Kapok is treated with hydrochloric acid. In this country excellent results have been obtained by digestion of corn cobs with 20 to 30 per cent sulphuric acid. According to Mains¹ the hydrochloric acid process may be disregarded because of its commercial impracticability for producing furfural at a very low price. The distillate from the digestion is fractionally distilled and the furfural separated. If an appreciable quantity of sulphuric or sulphurous acids is carried over during the digestion, resinous substances tend to form on heating. Resinification may be prevented by partial neutralization of the liquors before distillation.

The work of Roger Adams, Kamm and Marvel,² of Monroe, of La Forge, and of Mains and Phillips³ has demonstrated the feasibility of securing furfural in large quantities from corn cobs. Thus the production of synthetic resins from furfural is brought within the realm of economic importance. A large demand resulting in the low cost of manufacture may bring furfural resins very strongly into competition with hard rubber products.

Manufacture from Corn Cobs.

The Bureau of Chemistry⁴ outlines one process of making furfural as follows:

Corn cobs and water are placed in an autoclave and steam at about 135 pounds pressure is admitted. After cooking about two hours the furfural is blown off with steam, condensed, and collected as a dilute solution of furfural

¹ Chem. Met. Eng. 1922, 26, 779 and 841; Color Investigation Laboratory, Bureau of Chemistry.

² Univ. Ill. Bull. 1919, 16, No. 43, 5; J. Ind. Eng. Chem. 1921, 13, 133; W. S. Pat. 1,357,467; J. Ind. Eng. Chem. 1918, 925; Chem. Age 1920, 332.

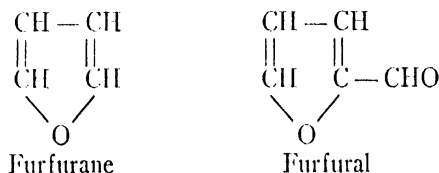
³ Chem. Met. Eng. 1921, 24, 661.

⁴ Preliminary information sheet issued July 3, 1922, by the Color Laboratory.

in water. The furfural is separated from the water in a specially designed distillation apparatus. A yield of about 6 per cent or 120 pounds of furfural per ton of cobs is now being obtained.^a

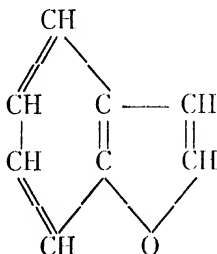
Properties of Furfural.

Although an aldehyde, furfural possesses an individuality which offers striking differences from the simple aldehydes, formaldehyde or acetaldehyde.^b This may be ascribed to the presence of the furfurane group. Furfural is an aldehydic derivative of furfurane (furan)



The cyclic compound, furfurane, may be looked upon as a member of the ethylene oxide series, which embraces many reactive compounds. Furfurane, itself, is highly reactive. Dimethyl furfurane is converted into a resin on treatment with strong mineral acids.

It should be noted that cumaron (see Chapter 2), a substance readily polymerized to a resin by strong sulphuric acid or aluminum chloride, is a furfurane derivative, benzene furfurane.



The addition to furfurane of an aldehydic group to form furfural secures a further degree of reactivity. In its reactions, furfural may function as an aldehyde, or as a member of the ethylene oxide series, or the properties of both groups may manifest themselves simultaneously. In consequence the reactions of furfural are many and diverse. It exhibits a facility of combination with other substances comparable in some respects to formaldehyde. Like the latter substance, it combines with phenols, ketones, amines and other bodies to produce resins.

^a Furfural is made by the Miner Laboratories, Chicago, Ill., on a commercial scale using a process of dilute acid digestion of oat hulls in rotary digestors. *Chem. & Met. Eng.* 1922, 27, 300. A bibliography of furfural is furnished by Miner, Trickey and Brownlee, *Chem. Met. Eng.* 1922, 27, 363.

^b In its reactions, according to Miner, Trickey and Brownlee, furfural resembles formaldehyde on the one hand and benzaldehyde on the other. *Chem. Met. Eng.* 1922, 27, 299.

Of course furfural differs strikingly from formaldehyde in several important respects and the furfural resins likewise are not similar to those made with formaldehyde. Hence the data on resinification obtainable on the one aldehyde are not directly applicable to the other. Like acetaldehyde, furfural may combine with itself to a resinous substance. Some of the resins are soluble and fusible, others are insoluble and infusible. The resins are mainly dark-colored products.

Historical.

Early in the course of research work carried out on furfural, the observation was made that resinous masses could be obtained by reaction with amines or phenols. Stenhouse,⁷ in 1840, and Fownes,⁸ in 1845, called attention to the formation of resinous bodies when furfural was boiled with acids or alkalis. Persoz⁹ and Stenhouse¹⁰ obtained gummy and tarry substances while working with furfural and aromatic amines and phenols. Claisen,¹¹ a few years later, produced a brown resin of indefinite composition when furfural was treated with β naphthol in glacial acetic acid solution, using hydrochloric acid as a condensing agent. In none of these cases was any study reported either of the reaction or of the resinous product aside from a very superficial examination of physical properties.

The reactions of furfural yielding resinous substances are greatly facilitated by the presence of catalyzers. The resultant resin varies in its properties depending on the character of the catalyst.

Furfural and Phenols.

The behavior of the phenols with furfural offer an interesting field for the investigator. While the work heretofore carried out on formaldehyde gives some indication of the manner of handling the reacting materials, as stated, furfural possesses a striking chemical individuality and its properties require further study to secure entirely controllable results.

In the reaction between furfural and phenols especially with acid catalyzers the tendency is toward the production of an infusible insoluble product. More often these are of a rubbery non-resinous nature. They show a decided degree of elasticity under compression but possess no tensile strength, resembling factis made by treating vegetable oils with sulphur chloride. The products of reaction with the acid catalysts are almost wholly brown or black in color. Aqueous hydrochloric acid, for example, added to a mixture of about equal parts of furfural and ordinary phenol brings about a violent reaction, the product being an elastic jelly-like product or a hard infusible brittle resin, the precise nature of the resulting material depending upon the amount of hydrochloric acid, temperature and other conditions. The black infusible elastic or resinous product forms irrespective of the amount of hydrochloric acid used. As the utility of a resin depends

⁷ Ann. 35, 301.

⁸ Ann. 54, 52.

⁹ Wagner's Jahresberichte 1860, 487.

¹⁰ Proc. Roy. Soc. 1870, 18, 537.

¹¹ Ann. 1887, 237, 272.

upon its being soluble or fusible so that it may be used either in varnishes or plastic products the furfural resins made with acid catalysts would have a very limited use if no means were at hand to check the reaction. Beckmann and Dehn¹² have taken advantage of the reaction with acid catalysts, thereby producing cast articles.¹³ They mix furfural, phenols and hydrochloric acid and pour the mixture into a mold. If the mixture is properly proportioned so that the reaction does not become violent and cause gases or steam to be evolved, a rigid, infusible, cast article is obtained. This procedure is, of course, of limited application. Moreover the hydrochloric acid used by Beckmann and Dehn as a catalyst acts on the metal walls of the mold and causes the casting to stick thereto.

Fusible Resins.

What is desired in a primary form of furfural resin is a soluble, fusible product which, in solution, may find application in various ways and which in molding compositions can be compounded with substances which bring about reaction under heat and pressure to cause setting or curing. In the employment of an acid catalyst a soluble, fusible resin will result only by the use of a large excess of phenol and removing the excess after the fusible resin is formed. Beckmann and Dehn found equal parts of furfural and phenol to represent approximately the combining proportions for resinification. Used in these proportions any addition of hydrochloric acid or other strong mineral acid, e.g., sulphuric or phosphoric acid, gives an infusible product. If ten times as much phenol as furfural is used with a hydrochloric acid catalyst a liquid is obtained from which the phenol in excess may be removed by heating, or distillation with steam, leaving a black fusible resin. Care should be taken not to greatly exceed this proportion of furfural as with, for example, 20 per cent of furfural, the infusible rubbery substance may form. Once this rubbery material is produced no means are known at present for its conversion into any workable form. The range therefore with furfural and ordinary phenol and hydrochloric acid catalyst is approximately between 10 and 20 per cent of furfural based on the phenol employed.

With this knowledge of the properties of furfural it may be assumed that mere dilution of the raw materials in a common solvent

¹² Sitzb. Kgl. preuss. Akad. Wiss., Berlin, 1918, 1201.

¹³ Baeyer, in 1872, treated phenol, resorcin and pyrogallol with furfural and hydrochloric acid. A trace of the latter produced an indigo blue substance soluble in water and precipitating as blue flocks on the addition of more hydrochloric acid. *Berichte* 1872, 5, 25. Steinitzer, German Pat. 305,624, June 10, 1917, obtained hard rubber substitutes from furfural, phenol and an acid catalyst, e.g., concentrated sulphuric acid or hydrochloric acid gas. 100 grams furfural, 50 to 100 grams phenol and 3 grams of sulphuric acid are heated slowly in a closed mold to 150° C., or hydrogen chloride is introduced into a mixture of furfural and phenol until an increase in viscosity is observed. Note also Swiss Pats. 85,076 and 86,308.

is all that is necessary to yield a fusible soluble resin. Although dilution through the use of phenol in excess enables this result to be achieved, such is not the case with many other organic vehicles applied as diluents. Experiments made by the author show a number of organic solvents, e.g., acetone, fail to serve as diluents of a character permitting the formation of the fusible resin. Thus the action appears to be a specific one for phenol and a few other substances, and a considerable amount of experimental work may be necessary in order to determine which substances are best adapted to this end. The procedure involving the employment of a phenol diluent somewhat increases the cost of operation.

Alkaline Catalysts.

A means of carrying out the reaction with approximately combining proportions of the raw materials to form soluble, fusible resins is found in the employment of alkaline catalysts. The resins obtained in this way have a far greater commercial significance than those yielded by acid catalysts. The resins obtained by alkaline catalysts will be discussed later in the chapter.

Anhydrous Reagents.

In making a resin of the phenol-formaldehyde condensation type aqueous formaldehyde ordinarily is used because paraform or hexamethylenetetramine are considerably more expensive so that they are used only in the finishing step of hardening the condensation product during the molding operation. The use of aqueous formaldehyde calls for removal of the water from the soft resin first obtained during condensation. Furfural has the advantage of being obtainable substantially free from water and hence, when caused to react upon phenol in the presence of an anhydrous acid catalyst, there is practically no water to interfere with the reaction other than that formed in small quantity during the condensation.

Substances Yielding Acids.

Saline compounds capable of liberating hydrochloric acid act as catalysts. Ammonium chloride functions weakly in this manner, but neither sodium nor potassium chloride serve as catalysts. Aniline hydrochloride is a very promising catalyst. The action is much like that of hydrochloric acid alone but is not so violent. Infusible resins generally are formed, however. The Bakelite Gesellschaft (Berlin) in addition to acids recommend organic halogen compounds capable of splitting off halogen acid. They propose the use of epichlorhydrin, acetylene tetrachloride and carbon tetrachloride. Thus furfural and phenol are mixed with the catalyst and the mixture is slowly heated in a closed mold to a temperature of 150° C. Cresol also may be used.^{13a}

^{13a} Swiss Pats. 85,076 and 86,308; Kunststoffe 1921, 62.

A fusible resin prepared by means of an alkaline catalyst or by employing a sufficient excess of phenol and an acid catalyst may be rendered infusible by heating with formaldehyde and an alkaline catalyst. Hexamethylenetetramine also is suitable for this purpose. Molded products of a heat-resistant character may be produced by hot pressing. When the fusible resin is prepared in the presence of an acid catalyst, the molded articles ordinarily are black and infusible, resembling hard rubber. In the products made from phenol and formaldehyde requiring a black color it is customary to introduce lampblack or other black coloring agent. When used for electrical purposes care must be taken to avoid the use of a coloring agent which will impair the electrical insulating properties of the molded material. Hence lampblack or carbon black are not always permissible. The normal jet black color of the furfural resin yielded by an acid catalyst makes the addition of any black coloring agent unnecessary and in some respects this is an advantage over the resins obtained by phenol formaldehyde condensation. On the other hand the furfural resin cannot be used when molded articles light in color are desired. The resin obtained by reaction in alkaline media is not as deeply colored as that yielded by acid condensation.

Work of Beckmann and Dehn.

Details of some of the researches of Beckmann and Dehn referred to previously⁴ will be of interest to chemists undertaking investigations on the properties of furfural-phenol resins. Beckmann and Dehn found when concentrated hydrochloric acid (39 per cent) is added to a solution of phenol and furfural that a reddish-violet color first appears, soon changing to a dark blue. The mixture becomes hot and finally solidifies to a black hard product which in acids and alkalis is completely insoluble and is not affected even by boiling. Likewise various organic solvents such as alcohol, chloroform, acetone and benzol are without action. The hardness of the product corresponds to Bakelite C. It is scratched by gypsum only weakly and by caespar strongly. It possesses a certain degree of elasticity, making it correspondingly difficult to break and the broken surfaces show a conchoidal fracture similar to hard resins. The resin may be turned satisfactorily in a lathe but attacks metal on account of its acid and phenol content. This objection may be overcome by heating, which makes the substance harder but more brittle.

In order to determine its composition a weighed amount of phenol and furfural was treated with hydrochloric acid and the solid material obtained was pulverized. The excess of phenol was extracted with hot water and the quantity determined. It was found however that repeated extractions and grinding did not suffice to completely remove the phenol so the method was abandoned.

Tests then were made by mixing phenol and furfural in various proportions to see if from the behavior of these mixtures the most reactive proportions could be determined. The following table gives the results of these observations. 10 per cent of concentrated hydrochloric acid was used as a catalyst.

The mixture containing 50 per cent furfural was the first to solidify. This was followed by the 60 per cent, 40 per cent, 75 per cent and 30 per cent. After about 24 hours the mixture containing 20 per cent of furfural solidified. The mixture containing 10 per cent of furfural remained liquid for a considerable time. Thus the effect of a substantial excess of phenol in preventing the formation of insoluble products is shown. The condensation progresses in a peculiar manner, in that after addition of hydrochloric acid solidification takes place along the walls of the vessel and at the surface of the liquid. The

⁴ Sitzb. Kgl. preuss. Akad. Wiss. Berlin, 1918, 1201.

remainder solidifies more slowly and is softer than the outer shell. This is readily noticed on turning in a lathe. On breaking a specimen the interior portion is found to have a dull surface of fracture while that of the outer zone is lustrous.

From the foregoing observations it was concluded that a mixture of equal parts of phenol and furfural was best adapted for further study with hydrochloric acid. Such a mixture was treated with 0.5 per cent of concentrated hydrochloric acid. As this was still a thin liquid after two days a further addition of 0.1 gram hydrochloric acid was made. This also remained liquid. Another quantity of hydrochloric acid of like amount was added and on 4 days standing a syrup was obtained which became a soft solid in about 3 weeks. Further hardening progressed very slowly. If however to the mixture of phenol and furfural $2\frac{1}{2}$ per cent or more of concentrated hydrochloric acid is added all at one time the condensation very readily progresses to completion. The rate of reaction increases with the concentration of the acid. With $2\frac{1}{2}$ per cent of hydrochloric acid the mixture remained liquid for two days, then gradually became gelatinous, and finally harder. The mixture with 5 per cent and 10 per cent of hydrochloric acid solidified in an hour and in a day was completely hardened. The addition of 15 or 20 per cent of concentrated hydrochloric acid to mixtures of equal parts of phenol and furfural quickens the reaction still more and a solid hard product is obtained in half an hour when the mixture is cooled by water. Without water-cooling the reaction occurs in about 2 minutes and in an almost explosive manner, affording a vesiculated brittle substance.

Other hydroxyl containing aromatic compounds react with furfural in the presence of hydrochloric acid. The following indicate some of the reactions reported by Beckmann and Dehn.

1. *Orthocresol*. The solution becomes blue violet and heats spontaneously soon solidifying to a black product.
2. *Metacresol*. This likewise heats but becomes dark blue and condenses to a black solid.
3. *Paracresol*. The solution first becomes green, then gradually blue and finally black. It remains liquid longer than the two other cresols but condenses to a solid substance. No spontaneous heating.
4. *Crude Cresol*. (From tar oil.) The solution heats strongly becoming reddish violet and after about an hour forms a hard black substance.
5. *Thymol*. The solution changes from blue to black and soon thickens to a solid. There is no spontaneous heating.
6. *Pyrocatechin*. The solution goes gradually with spontaneous heating from a reddish violet to blue and then black. The separated solid condensation product is lustrous and shows a slight separation of pyrocatechin.
7. *Resorcin*. The solution reacts immediately and in a violent manner on the addition of hydrochloric acid. Ebullition occurs and a solid substance separates which is full of bubbles.
8. *Hydroquinone*. One part of hydroquinone dissolves completely in an equal amount of furfural only on heating. Hydrochloric acid was added to the warm solution and after cooling a solid black substance was found to the surface of which some separated hydroquinone was clinging.
9. *Guaiaicol*. At the beginning the solution is brown but becomes black remaining liquid for a long time and finally solidifying to a product which has an excellent appearance. No spontaneous heating.
10. *Pyrogallol*. Reaction takes place violently with blackening and the rapid formation of a vesiculated mass.
11. *Phloroglucin*. Dissolves in furfural only on heating and the addition of hydrochloric acid to the hot solution brought about a violent reaction with ebullition and separation of a vesiculated brittle substance.
12. *Metachlorphenol*. The solution becomes dark green and reacts slowly, condensing finally to a hard lustrous solid but without any indication of heating.
13. *Parachlorphenol*. The solution becomes a dirty gray and eventually black with the separation of a soft and friable substance, no heating being observed.
14. *Orthonitrophenol*. A yellowish green oil separates which remains liquid and shows only slight indications of black particles. There is no evolution of heat.
15. *Paranitrophenol*. The solution becomes brown and then black without the evolution of heat. It remains liquid for a long time but finally solidifies to a product which is not homogeneous. It is admixed with unchanged nitrophenol and is very friable.
16. *Picric Acid*. Even on warming shows no visible reaction. The dark green mixture remains liquid.
17. *Para-aminophenol*. This dissolves in furfural only on heating and reacts even without the addition of any acid.

18. *Menthol*. Produces a green solution which grows darker on warming and later becomes black. Finally a black spongy mass separates which even after a considerable period does not become solid.

19. *Terpineol* affords a brown solution which does not change in appearance immediately; later, however, it turns red and a solid forms without spontaneous heating.

20. *Carvacrol* yields a reddish violet solution which soon heats spontaneously and after 2 hours is solid. The product is fairly hard.

21. *Camphor*. The solution reacts very slowly with a reddish violet coloration, gradually becoming brownish.

22. *Borneol*. Borneol 1 part dissolves completely in the cold in 2 parts of furfural. The solution is colored violet on the addition of hydrochloric acid, then brownish-black while a solid substance separates. There is no self-heating and unchanged borneol remains.

23. *Alpha naphthol*. The solution immediately becomes a beautiful red color turning to a violet and with a violent, almost explosive reaction changing to a solid black substance. The product is unusually hard but vesiculated.

24. *Beta naphthol*. Reacts immediately with the appearance of a dark blue coloration but the reaction is less violent than in the case of alpha naphthol; however, there is a strong evolution of heat. The reaction product is hard and lustrous.

Substitution in para position as regards the hydroxyl group appears to be unfavorable for condensation.

Of the foregoing products the most promising ones were from phenol, crude cresol, guaiacol, carvacrol and beta naphthol; all made in the proportion of 10 parts furfural, 10 parts of the phenolic substance and 1 part of concentrated hydrochloric acid. In manufacturing these resins on the large scale, of course only the products from phenol and crude cresol or possibly naphthol can be considered. The others are too expensive.

In place of aqueous acid, alcoholic hydrochloric acid may be used to produce black bodies of great firmness. These have a conchoidal fracture and machine well but differ from those made with the aqueous acid in having a lustrous surface of fracture throughout the mass instead of having the outer zone only of lustrous material.

Equal parts of phenol and furfural treated with 10 per cent of a methyl alcohol solution of hydrochloric acid immediately became dark blue, heating spontaneously and then turning black. However the reaction did not appear so violent as with the aqueous acid. The next day the mixture was found to be a solid lustrous product. Because of strong contraction the product had separated completely from the walls of the vessel. The surface was moist, which was indicative of the formation of water during the condensation. The excess of hydrochloric acid and uncombined phenol and furfural were removed through careful heating to a temperature not exceeding 60° C. If a higher temperature was employed splitting occurred.

A mixture of equal parts of crude cresol and furfural, to which ethyl alcohol containing hydrochloric acid was added, produced immediately a violent reaction. In spite of cooling with water the combination was so vigorous that the solid product obtained was full of bubbles. The reaction goes on even more violently with gaseous hydrochloric acid. Other halogen acids, especially hydrofluoric acid, act like hydrochloric acid. The reaction is slow with concentrated hydriodic acid. Other inorganic acids such as sulphuric and phosphoric acid also give solid condensation products. Organic acids such as acetic, tartaric and benzoic acid, show very little tendency to form condensation products and the solution remains liquid even after heating for a long time. The mixtures treated with acetic and benzoic acid did not show a black coloration.

Trickey, Miner and Brownlee¹⁵ found oxalic acid to be less active than sulphuric or hydrochloric acids. External heat was necessary to cause the reaction to proceed. The results of Miner's observations on hydrochloric acid as a catalyst are summarized as follows:

1. In order to obtain an infusible insoluble resin the molecular proportions preferably should be slightly in excess of one mol. furfural to one mol. phenol.

¹⁵J. Ind. Eng. Chem. 1923, 65.

2. The resin obtained by an excess of phenol was soluble in acetone and alcohol, and remained a jelly-like mass when cooled, even after it had been heated for a number of days.

3. The resins obtained by use of varying amounts of acid as a condensing agent were similar, but the time necessary to complete the reaction varied from two weeks in the case of 0.2 per cent to 10 hours in the case of 0.6 per cent acid, indicating that the acid catalyst is most effective within a very narrow range of concentration.

Chlorides as Condensing Agents.

In view of the activity of hydrochloric acid various halide compounds were tried by Beckmann and Dehn. Numerous investigations show that the more loosely bound the hydrochloric acid the more active the compound. Thus sodium or potassium chloride even after prolonged boiling had no action. Ammonium chloride and the amines on the contrary bring about reaction. Ten per cent of ammonium chloride added to mixtures of furfural and phenol, crude cresol or alpha naphthol causes a reaction with the appearance of a black coloration on heating. However, these mixtures remain liquid even after prolonged boiling. On the contrary, if the hydrochloride of aniline or hydroxylamine is used the condensation goes to the ultimate stage. A furfural mixture to which 10 per cent of hydroxylamine hydrochloride is added and heated reacts violently with the formation of a black solid product. Aniline hydrochloride when used upon phenol-furfural mixtures is somewhat slower so that constant heating to about 70° C. was found necessary. A mixture of 100 grams each of phenol and furfural and 30 grams of aniline hydrochloride required heating at the temperature named for a period of 30 hours to bring about complete condensation. The condensation did not go on uniformly. After 20 hours a part of the mixture had completely solidified while the remainder was liquid. Some of the liquid spread in a thin layer on a glass plate exhibited globules of water; a confirmation of the view that in the reaction water is liberated. The dark liquid on further heating solidified gradually and after another 10 hours the whole mass was a solid body. A fracture showed unequal condensation similar to that produced by the hydrochloric acid catalyst. Similar products were obtained from mixtures of equal parts of crude cresol or alpha naphthol with furfural, but in these cases the condensation progressed more readily and the mixtures reacted spontaneously after a brief warming. In fact cooling was necessary in order to retard the reaction.

Acid Chlorides.

Metallic chlorides of an acid character act similarly to the amine chlorides, zinc chloride and aluminum chloride being effective. A mixture of equal parts phenol and furfural with 10 per cent of zinc or aluminum chloride when heated turned black and condensed after 2 hours heating at 80° C. to a hard substance. The same result was

obtained with crude cresol or alpha naphthol. Equal parts of phenol and furfural treated with 1 per cent of cuprous chloride on long heating gave a solid black substance.

Condensation by Means of Bases.

The catalytic activity of strong mineral acids in converting mixtures of phenol and furfural into black infusible solids resembling hard rubber in general appearance has interested a number of investigators to such an extent that the valuable resins obtained by the action of alkaline catalysts have been largely overlooked in the past. Various proposals have been made to cast articles by means of an acid catalyst which could be used as substitutes for hard rubber. The acid catalyst is, however, not a very practical one to use in this manner and the later trend of development has been in the direction of employing alkaline catalysts to secure soluble or insoluble resins depending upon the proportions of the reacting constituents.

It is of interest to note that Beckmann and Dehn observed that a mixture of phenol and furfural darkens immediately on the addition of the basic catalyst but remains liquid or at best is converted into a brownish-black or black plastic mass melting at about 150° C. and soluble in many organic solvents. Thus they report that a mixture of equal parts phenol and furfural was treated with caustic soda solution, carbonate of soda solution and aqueous ammonia, and on heating formed a brown oil. When the mixture was heated for 8 hours at 180° C. in a sealed tube it became thicker. The ammonia solution yielded a plastic mass, which was soluble in hot alcohol and which dissolved completely in acetone and chloroform in the cold. It was especially resistant to acids and alkalis.

Similar products were obtained by Beckmann and Dehn when furfural-phenol mixtures were treated with solid alkali hydroxides or carbonates. For example, phenol, crude cresol, and alpha or beta naphthol with an equal weight of furfural were treated with 10 per cent of sodium or potassium carbonate in powder form. On heating, the mixture evolved carbon dioxide, becoming dark brown and thick. The phenol-furfural and the crude cresol-furfural mixtures after heating for 3 hours to 100° C. solidified to brown gummy masses. These were soluble in organic solvents and when dissolved in alcohol or benzol produced a clear brown varnish. They melted easily and on heating to higher temperatures passed over into infusible and insoluble substances similar to those obtained by means of acids or chlorides. The alpha naphthol-furfural mixture required heating to start the reaction and then the reaction progressed violently so that cooling with water was necessary. The black granular condensation product was completely soluble in alcohol and the solution on evaporation afforded a yellowish-green lustrous surface which in the air and on heating gradually became brown. With beta naphthol the corresponding reaction was much slower, only after 4 hours heating to 100° C. was the composition solidified.

Trickey, Miner and Brownlee¹⁶ found, contrary to Beckmann and Dehn, that infusible resins could be obtained readily when alkaline condensing agents were employed. The results are summarized as follows:

¹⁶J. Ind. Eng. Chem. 1923, 65. Meunier also has obtained resinous products from phenol and furfural in the presence of bases or basic salts. The products are intended for use in the production of varnishes. French Pat. 23,821, addition to French Pat. 472,384. *Kunststoffe* 1922, 12, 164.

1. In order to obtain an insoluble resin the proportions are preferably about 1.25 mols furfural to 1 mol phenol.

2. The resins formed by excess of phenol were solid and brittle when hot, melted easily, and were readily soluble in acetone, alcohol and furfural. When heated with enough furfural to bring the molecular proportion up to 1.25 furfural to 1 phenol the resin went over to the infusible state. With these resins excellent cold molded products were produced on a commercial scale.

These investigators reported that 1 per cent of the mono hydrate of sodium carbonate figured on the total weight of the mix gave a reaction mixture that was easily controlled. Sodium hydroxide also was used with good results. The author has employed sodium or potassium carbonate in experimental work on furfural resins and prefers a somewhat larger proportion to that stated. Thus a mix composed of 100 parts by weight of phenol, 75 parts of furfural and 10 parts of sodium carbonate, when heated under a reflux condenser to about 150° C. for 3 hours, yields a dark brown resinous solid which is readily soluble in an equal weight of denatured alcohol. Any excess of phenol or furfural may be removed by blowing with steam for several hours at 170° C.

Resins made with alkaline catalysts in this manner are too dark-colored for most applications in the varnish industry and therefore their uses in this field are quite limited. In the production of plastic materials they have qualities so different from those of the phenol-formaldehyde type of synthetic resin that probably a considerable amount of investigation is necessary in order to adapt the furfural product to molding purposes of the character demanded in the resinous phenol-formaldehyde condensation products. The furfural resins do not show the same reactivity when incorporated with hexamethylenetetramine, hence hardening does not take place rapidly in the mold and a great deal of difficulty arises from sticking to the mold. The phenol furfural resins have been applied successfully in the manufacture of printing plates and matrices, but in this application it is customary to interpose a thin sheet of tinfoil between the mold and the molded piece. The foil prevents sticking difficulties. On the other hand, a well-cured phenol-furfural plastic made with wood flour filler possesses good strength and appearance.

A promising development in the use of phenol-furfural resins is that of cold molding described in Chapter 26. The plastic material is molded in the cold and then subjected to a baking operation lasting for several hours, which brings about a gradual hardening. Furfural resins appear to be very well adapted for the cold molding field although considerably more expensive than the pitches and asphaltic bodies commonly used.

Alkaline Salts.

Beckmann and Dehn report that, generally speaking, alkaline salts do not bring about condensation between phenol and furfural. Numerous tests were made with sodium perchlorate, perborate, thiosulphate, sulphite, etc., without noticing any condensation. The solutions became somewhat darker and colored on heating but remained liquid. Sodium peroxide acted immediately with an especially violent reaction and ignition of the mixture.

Condensation without Catalysts.

Mixtures of phenol, crude cresol or alpha naphthol and furfural will react without the application of any catalyzer. Beckmann and Dehn heated equal parts phenol and furfural in a sealed tube for 8 hours with the temperature rising to 220° C. The mixture became dark brown but remained liquid and was completely soluble in alcohol, acetone and chloroform. A solution of equal parts crude cresol and furfural when heated under the same conditions gave a thick brownish black oil which contained water globules. The oil was only partly soluble in alcohol but completely soluble in acetone, chloroform and benzol. When equal parts of alpha naphthol and furfural were heated in a sealed tube at 150° C. for 9 hours a solid product was obtained which as a result of the violent reaction was full of bubbles. On heating it softened without melting and was insoluble in alcohol, acetone, chloroform and benzol.

Modifying and Extending Agents.

Additions of glycol, glycerol, naphthalene, anthracene, vaseline, paraffin, ozokerite, rosin, cumaron resin and pyroxylin lacquer were not suitable and for the most part separated during condensation. Good results were obtained however with coal tar. A mixture of 4 parts phenol, 4 parts furfural and 1 part by weight of tar was dissolved by heating and on cooling was mixed with 1 part hydrochloric acid. The mixture reacted violently with ebullition and after a half hour was a solid, but as a result of the violent reaction was vesiculated and brittle. To lessen the vigor of the reaction a second mixture likewise prepared was immediately cooled with water after the acid was added and only after it had become solid, which required about half an hour, was it raised to 60° C. This product could be turned well in a lathe. Still better results were obtained by the use of lanoline, 5 per cent being suitable. A solid black body was formed which was very elastic. This elasticity was maintained even on heating to 100°.

Sulphur.

In view of the great similarity of solid phenol-furfural condensation products to hard rubber the condensation product was treated with sulphur. No beneficial effect could be found through such treatment. In fact the resin was more brittle than the product made without sulphur.

Fillers.

Better results were obtained when fillers such as infusorial earth, wood flour, asbestos, etc., were added. For example an acidified solution of 1 part phenol in 1 part furfural was ground with 2 parts of kaolin and the mixture allowed to condense while cooling with water. The product was homogeneous and on drying did not show cracks. It was however more brittle than the pure condensation product and broke when allowed to fall on a stone floor. A mixture of asbestos gave better results, 1 part of fine fibred asbestos being added to a solution of 5 parts each of phenol and furfural, which was acidified with hydrochloric acid. The mixture was cooled with water.

Phenol, Furfural and Formaldehyde.

Equal weights of phenol, formaldehyde and furfural were mixed with 10 per cent of concentrated ammonia and on boiling a dark brown oil separated, as in the case of the furfural mixture alone. The alkaline reacting liquid was heated in a sealed tube at 180° C. for 3 hours and a mixed brown and black colored vesiculated product was obtained. With 10 per cent of aniline hydrochloride, by the same procedure somewhat more homogeneous products were obtained than those made with ammonia. They were however moist and spongy. It is better therefore to carry out the condensation at 80° C. and at atmospheric pressure. The product in that case is as hard as when made by acid condensation but it must be very carefully dried. More unfavorable results were obtained when in place of formaldehyde other aldehydes such as benzaldehyde were used.

Benzaldehyde.

A mixture of phenol, furfural, benzaldehyde and concentrated hydrochloric acid colored reddish violet and spontaneously heated, turning gradually black and viscous. The condensation did not form a product as solid as would have been the case if benzaldehyde were absent but yielded a soft spongy mass which was partially soluble in organic solvents. A similar but somewhat more solid body was obtained when cresol was used in place of phenol. Aniline hydrochloride, as a catalyzer, afforded only liquid products.

Impregnation of Paper, Molded Articles, etc.

Beckmann and Dehn impregnated paper with furfural and phenol containing 1 to 2 per cent of hydrochloric acid. After standing for two days, then heating, a waterproof hardened sheet was obtained which possessed good insulating properties. The acid used did not cause the paper to become brittle. Solutions of the resin in organic solvents also were employed for impregnating paper. When the resin, prepared with an acid catalyst, was allowed to set in contact with metal the adhesion was pronounced and handles were readily cast on files, screw-drivers, etc. The metal surface was protected from action of acid by a coating of asphalt varnish. To the furfural mixture 10 to 20 per cent of concentrated hydrochloric acid was added and the whole poured into a container in which the tool handle was placed. The mold was cooled by water. The next day the articles were removed from the molds and were heated to 80° C. for a short time to remove uncombined materials. Handles resembling hard rubber resulted. Their insulating properties were not satisfactory and could not be much improved by treatment with alcoholic ammonia. A better degree of electrical resistance was shown by articles made with aniline hydrochloride as a catalyst. These required keeping for some time in order to insulate against a high tension spark. Using 10 to 15 per cent acid catalyst and water-cooling, plates were made which were strong and elastic. They could be thrown against stone without breaking, and with a screw press the impression of a coin could be neatly made in the surface. Soles for shoes were produced from this stock.

Furfural also has been proposed as an agent for hardening soft pitches or resins. The latter are heated in the presence of mineral or organic acids with furfural. The heat treatment is carried out either under a reflux condenser or under pressure. The resulting product is washed and dried. The melting point of the hardened resin may be raised by melting it under reduced atmospheric pressure or by blowing it with air at 180-350° C.¹⁷

Novotny and Kendall¹⁸ apparently follow the teachings of Beckmann and Dehn in preparing phenolic condensation products with furfural in place of formaldehyde.

¹⁷ Plauson, German Pat. 352,521, 1920; J. S. C. I. 1922, 41, 720A.

¹⁸ U. S. Pat. 1,398,146, Nov. 22, 1921; J. S. C. I. 1922, 41, 66A; Chem. Abs. 1922, 16, 843.

A fusible resin first is prepared by heating under pressure 100 parts of phenol with 15 to 40 parts of furfural and 5 to 10 parts of hydrochloric acid of about 39 per cent strength. The phenol crystals are melted and then the furfural and the hydrochloric acid catalyst are added. Considerable heat is generated and the pressure vessel therefore is water jacketed. A temperature of about 93° C. (200° F.) is maintained. The mixture is subjected to agitation under these conditions for a period of about one hour, or for a sufficient length of time to allow combination of all the furfural. The vessel is then subjected to a higher temperature (166° C., 330° F.) to separate the hydrochloric acid and water of condensation. Any excess of phenol may be eliminated by steam or vacuum distillation. An alkali may be added to remove any trace of hydrochloric acid. The fusible resin obtained is then mixed with a hardening agent such as furfuralamide, 8 to 40 per cent of the latter being added. The observation is made that furfural itself may be used as a hardening agent, in which case a catalyst is required. Ammonia is recommended for the purpose. Furfuralamide liberates ammonia during the reaction. The fusible resin may be in the form of a powder or in solution in alcohol or acetone when treated with the hardening agent and under pressure the dry composition sets to a rigid infusible condition on being subjected to a temperature of 93°-177° C. (200°-350° F.).

Hexamethylenetetramine may be used as a hardening agent, 5 to 20 per cent being recommended. A phenol-formaldehyde resin may be obtained by the treatment of 100 parts of phenol with 55 parts of 37 per cent aqueous formaldehyde solution. The fusible resin formed is treated with furfural or furfuralamide as a hardening agent, using about 8 to 40 per cent, based on the weight of the fusible resin employed. Likewise acetaldehyde or paraldehyde may be allowed to react on phenol in the proportions by weight of 100 parts of phenol to 37 parts of aldehyde, in the presence of ½ to 1 per cent of hydrochloric acid calculated on the total weight of the batch. Furfural or furfuralamide is added as the hardening agent, the proportion of 15 to 40 per cent being employed.

These resinous compositions may be incorporated with a fibrous filler, corn-cob cellulose being recommended for the purpose.

Furfural resins have been used by Novotny in the manufacture of printing plates¹⁹ for phonograph records²⁰ and for producing a moldable composite body;²¹ in each case furfural and phenol condensation products are used to impregnate paper, cloth or other fibrous material; the product being made into a sheet-like form adapted for molding purposes.

Amines and Furfural.

Aniline.

In 1916 Meunier²² published details of his work on various furfural resins including a product obtained with aniline. Equal volumes of aniline and furfural were heated in a closed vessel for 48 hours at 70-80° C. or 3 hours at 140-150° C., affording a resin soluble in benzol and alcohol. A 15 to 20 per cent solution of the resin in benzol when applied as varnish gave a brilliant black coating. When spread over a surface and heated even moderately (50-60° C.) an insoluble black enamel is obtained.

¹⁹ U. S. Pat. 1,377,519, May 10, 1921.

²⁰ U. S. Pat. 1,398,148, Nov. 22, 1921.

²¹ U. S. Pat. 1,398,147, Nov. 22, 1921.

²² Les Matières Grasses 1916, 4516.

The reaction can be accelerated by adding a dehydrating agent such as zinc chloride.²³ Mains and Phillips²⁴ have made a more extended examination of the conditions under which the resins described by Meunier are formed, and have studied the formation of soluble resins by the condensation of furfural with a number of other compounds.

The method of attack was to determine first the optimum concentrations of amine (or other compound under test) and furfural for the formation of a resin at room temperature, approximately 25° C. Where no resins at all were obtainable at room temperature the optimum concentrations were determined at 100° C. Using the concentrations which gave the best results in the previous experiments, resins were made at 25° C., 100° C. and 150° to 200° C. Having determined the optimum temperature, the length of time necessary under the given conditions to form the most satisfactory resin was similarly investigated. The resins obtained were not pure compounds, but products of an indefinite and varying composition, and the same consistency of resin was produced over a rather broad range of temperature by varying the length of heating period. Their criterion of the quality of the resin was simply that it should be hard and fairly brittle when cooled to room temperature and yet not be noticeably carbonized. Mains and Phillips confirmed the findings of Beckmann and Dehn that hydrochloric acid is an exceedingly effective catalyst in producing resins from furfural. It not only effectively catalyzes the formation of both fusible and infusible types of resins from furfural and other compounds, but added to furfural alone causes the formation of an infusible resin.

The results obtained with each compound follow, the reactions being carried on in an open flask unless otherwise stated, and all proportions being given by weight.

Aniline. Equal parts of furfural and aniline heated for one hour at 200° C. in an open flask or for three hours at 170° C. in a flask attached to a reflux condenser give a black resin, hard and brittle at 25° C.

Aniline Hydrochloride. Equal parts of furfural and aniline hydrochloride heated at 100° C. for one hour produce a black resin, hard and brittle at 25° C.

Aniline plus Hydrochloric Acid. Five parts each of furfural and aniline and one part of concentrated hydrochloric acid, specific gravity 1.19, give a resin similar in characteristics to the above in 10 minutes at 90° C.

m-Nitraniline. By heating one part of furfural and two parts of m-nitraniline at 150° C. for one hour and fifteen minutes a black resin becoming hard and brittle at 25° C. may be obtained. If the temperature exceeds 175° C. a violent reaction occurs giving off voluminous clouds of dense brown smoke.

Cymidine plus Hydrochloric Acid. Five parts of furfural, 5 parts of cymidine (1-CH₃, 2-NH₂, 4-isopropyl benzene) and one part of hydrochloric acid (specific gravity 1.19) heated at 150° C. for ten minutes give a dark reddish brown resin very hard and brittle at 25° C. Without the presence of hydrochloric acid no resin is formed even after heating for three hours at 200° C.

α-Naphthylamine. When heated for three hours at 200° C. one part furfural and two parts α-naphthylamine condense to form a black resin, hard and brittle at 25° C.

β-Naphthylamine. One part of furfural and two parts of β-naphthylamine mixed at room temperature, 25° C., give the immediate formation of a reddish-brown hard, brittle resin.

o-Toluidine plus Hydrochloric Acid. By heating five parts of furfural, ten parts of o-toluidine and one part of hydrochloric acid (specific gravity 1.19) for one hour at 150° C. a black resin is produced which is very hard and brittle at 25° C. Without the addition of the hydrochloric acid no appreciable thickening of the liquid is found even after heating for three hours at 200° C.

p-Toluidine. One part of furfural and two parts of p-toluidine heated for two and one-half hours at 150° C. produce a black resin becoming hard and brittle when cooled at 25° C.

m-Toluylenediamine. Equal parts of furfural and m-toluylenediamine, upon standing over night at room temperature, 25° C., give a dark brown, hard, brittle resin.

Xylydine plus Hydrochloric Acid. By heating five parts of furfural, five parts of xylydine (crude mixed) and one part of hydrochloric acid (specific gravity 1.19) together for fifteen minutes at 150° C., a very thick, dark red, almost black, resin is formed, very hard and brittle at 25° C.

²³ Cf. French Pat. to Meunier 472,384, Aug. 2, 1913; J. S. C. I. 1915, 435.

²⁴ Chem. Met. Eng. 1921, 24, 661. Note U. S. Pat. 1,441,598, Jan. 9, 1923, to Phillips and Mains.

Other Amines. No resins were formed by the action of furfural on amylamine, dimethylaniline, diphenylamine and m-phenylenediamine even after heating at 200° C. for three hours. Furfural condensed with the following at room temperature to form crystalline compounds: p-nitraniline, benzidine and toluidine.

Furfural and Ammonia.

Furfuramide Resins.

Meuniér (*l.c.*) treated furfural with aqueous ammonia to obtain furfuramide, $(C_5H_4O)_3N_2$, then heated the moist product in an autoclave to 120-140° C. for about 3 hours, or to 80-100° C. for 48 hours. This procedure afforded a brown resin easily soluble in benzol. The solution may be used directly as a varnish or the resin may be incorporated with linseed oil. The substitution of ammonium sulphhydrate instead of ammonia engenders a black resin of disagreeable odor.

Thiofurfural (see Chap. 19) is sometimes obtained in the form of a resin. The passage of hydrogen sulphide rapidly through a hot concentrated solution of furfuramide yields this substance in a resinous state. A corresponding selenium compound also is resinous.²⁵ The aliphatic amines also react in a manner similar to ammonia.

Mains and Phillips (*l.c.*) prepared furfuramide resin as follows:

Ammonium Hydroxide (Furfuramide Resin).

To an aqueous solution of furfural an excess of ammonium hydroxide is added. The furfuramide formed, partially dried and heated for one hour at 100° C., gives a reddish brown resin hard at room temperature. Trickey, Miner and Brownlee²⁶ report that the furfuramide resin of Mains and Phillips is impure furfuralin $(C_{15}H_{12}O_3N_2)$.²⁷

Furfural and Caustic Alkali.

Furfural resinifies in the presence of hot aqueous caustic alkali. To 1 part by weight of furfural Meuniér (*l.c.*) uses 7 parts of alkali solution, containing at least 20 pounds of caustic alkali in 120 pounds of the lye. The solution is heated to boiling in a closed kettle equipped with a reflux condenser. The furfural is added to the boiling solution. The lye turns dark brown and at the end of an hour the solution is

²⁵ Wurtz, Dict. d. chimie, Vol. I, Part 2, 1506; Baumann and Fromm, Ber. 24, 3591.

²⁶ J. Ind. Eng. Chem. 1923, 65.

²⁷ Note Dubosc (Le Caoutchouc et la Gutta-Percha 1920, 10495; Kunststoffe 1921, 11, 59), who found that furfuramide when fused in the absence of air yielded a brown resinous mass consisting for the most part of furfuralin. Bertagnini in 1853, Ann. Chem. Pharm. 88, 128, prepared furfuralin by heating furfuramide at 110°-120° for one hour, dissolving the resinous mass formed in alcohol, precipitating the furfuralin as the double oxalate. This compound is soluble in boiling water and is decolorized by treatment with animal charcoal at the boiling temperature, filtered hot and allowed to crystallize from the filtrate. The furfuralin is liberated by action of potassium hydroxide and obtained as a white crystalline compound.

acidified with hydrochloric acid which precipitates a black resin. Alcohol readily dissolves the resin and the solution may be used for coating purposes, affording, when dry, a firm, glossy black surface. The resin also may be employed in conjunction with linseed oil. A better yield of resin is obtained by heating in an autoclave to 140-150° C. instead of using a reflux condenser.

A somewhat similar procedure is followed by Mains and Phillips.²⁸ 1 part of furfural and 7 parts by weight of a 25 per cent sodium hydroxide solution are heated together for 1 hour in a flask attached to a reflux condenser. Concentrated hydrochloric acid (specific gravity 1.19) is then added in excess and a black resin separates, the excess of acid is washed out and a medium hard tar is formed which gradually becomes brittle upon standing.

Ketones and Furfural.

Acetone.

Meunier²⁹ recommends the employment of the reaction between furfural and acetone as a means of producing resins adapted for industrial uses. One procedure is as follows: 3.5 parts of a caustic alkali solution containing caustic potash or caustic soda, 1 part by weight, and water 2.5 parts by weight are brought to the boiling temperature in a receptacle provided with a reflux condenser. During the course of 15 minutes 1 part by weight of a mixture of equal volumes of furfural and acetone is added. About 15 minutes after the mixture of furfural and acetone has been introduced the boiling is stopped and a resin is found in the bottom of the container. The resin is washed, preferably while hot, with water acidified with hydrochloric acid and then dried. 100 pounds of furfural yield by this method 140 to 150 pounds of the dried resin. The product, after drying, is a yellow resin. A 20 per cent solution in acetone, benzol, or a mixture of 23 volumes of furfural and 77 volumes of alcohol serves as a varnish. The original caustic solution may be used over again to resinify additional quantities of furfural and acetone.

A harder and more transparent resin may be obtained by the following method: the caustic alkali solution is placed in an apparatus equipped with an agitator and the mixture of acetone and furfural is added slowly with cooling to prevent over-heating which would volatilize the acetone. The resulting mass thickens little by little until a hard, thick paste is found in the container. After removing the excess of alkali the resin is placed in an autoclave and heated for 4 hours at a pressure in the neighborhood of 15 pounds. By this method Meunier obtained a light-colored transparent resin, very soluble in benzol, acetone, and a mixture of alcohol and furfural as described above, giving in 20 per cent solution an almost colorless and very bril-

²⁸ Chem. Met. Eng. 1921, 24, 661.

²⁹ Les Matières Grasses 1916, 4516.

liant varnish. The resin alone or mixed with other resin, may be heated with linseed oil, to make an oil varnish.

The same procedure can be used to form a resin from oil of acetone or from aldehydes, particularly acetaldehyde.

Mains and Phillips use a stronger solution of caustic soda, otherwise the procedure is substantially the same as that used by Meunier.

One part by weight each of furfural and acetone and 2 parts of 50 per cent sodium hydroxide solution are heated in flask attached to a reflux condenser for 30 minutes at 100° C. condensing to give a dark brown solid mass. By washing out the excess alkali with dilute acid, drying at 100° C. and cooling to room temperature a hard, brittle, brown resin is formed.

Methyl Ethyl Ketone.

Five parts of furfural, 2 parts of methyl ethyl ketone and 5 parts of 50 per cent sodium hydroxide solution give almost immediately at room temperature, 25° C., a dark brown gum. By washing out the excess alkali with dilute acid, drying at 100° C. and cooling to room temperature, a hard brown resin is obtained.

General Properties of Resins Produced.

The resins do not have sharp fusion points, softening gradually till fluid. The softening temperatures of the resins made by Mains and Phillips lie between 25 and 100° C., but have not been carefully determined, since the softening point can be raised to almost any reasonable temperature desired by simply heating the resins at higher temperatures or for a longer period of time.

All of the above resins obtained by Mains and Phillips are practically insoluble in water. They are somewhat soluble in turpentine, quite soluble in benzol, acetone and alcohol, and very soluble in furfural.^{29a} The acetone, benzol and furfural solutions of these resins form varnish stains which, when applied to wood, give shades ranging from golden brown to black, depending upon the resin, the concentration of the solution and the number of coats applied. The surfaces thus coated have a glossy appearance.

Of the furfural resins described, those which are produced from cheap enough materials to be of possible practical importance at the present time are: furfuraniline, furfur- α -naphthylamine, furfur-*o*-toluidine, furfur-xyldine, furfur-acetone, furfur-methylethylketone, furfur-amide, and furfur-sodium-hydroxide resins.

The appearance of the varnish stains on white oak when the resins are applied in a single coat from the saturated benzol and furfural solutions is given in the following table.

^{29a} Tetralin is recommended as a solvent for furfural resins. J. S. C. I. 1922, 568R.

APPEARANCE OF FURFURAL VARNISH STAINS ON WHITE OAK

Resin	Shades Given by One Coat of Resin	
	Applied in Saturated Benzol Solution	Applied in Saturated Furfural Solution
Furfur-aniline	Light brown	Dark brown
Furfur- α -naphthylamine	Dark brown	Nearly black
Furfur-o-toluidine	Medium brown	Dark brown
Furfur-xylydine	Dark reddish brown	Dark reddish brown
Furfur-acetone	Golden brown	Dark brown
Furfur-methylethylketone	Golden brown	Golden brown
Furfur-amide	Reddish brown	Reddish brown
Furfur-sodium hydroxide	Medium brown	Dark brown

By allowing the furfural solutions to evaporate somewhat and applying several coats, furfur-aniline, furfur- α -naphthylamine, furfur-o-toluidine and furfur-xylydine resins give attractive black enamels. The furfur-sodium hydroxide resin also gives a black enamel, not quite as good as the others.

Montgomery and Ernst³⁰ have found that water solutions of furfural, as dilute as 2 per cent, mixed with aniline and heated to 125° C. in an autoclave for 15 minutes, yield resinous bodies similar to the "furfur-aniline" described by Mains and Phillips. The resin obtained from aqueous solutions by heating under pressure gives a darker shade, when applied to wood, than the resin obtained with anhydrous materials by Mains and Phillips.

When an excess of aniline is used with the solutions of furfural, the residue is oily and not brittle at 25° C., but when the mixture is steam distilled the excess aniline is separated and the residue is hard and brittle at 25° C.³¹

Cellulose and Phenol.

A curious method of obtaining resins is that of Glaessen,^{31a} who heats wood or wood waste with phenol in the presence of a small proportion of hydrochloric acid or other catalyst. The raw material, for example small pieces of wood, is heated with the phenol in some cases with a diluent such as water, alcohol or benzene. When sufficiently treated the cellulose is separated, any excess of phenol is recovered

³⁰ Chem. Met. Eng. 1921, 25, 335.

³¹ The preparation of water solutions of furfural is very easy, but the fractionation of the furfural is somewhat difficult (J. Ind. Eng. Chem. 1921, 13, 133) and there is always a considerable percentage, frequently up to 8 and 10 per cent, of furfural in the rejected water. If the furfural production is being carried on with a view to subsequent condensation with aniline, it would seem useless first to prepare pure furfural. If furfural is being prepared for other purposes, the rejected water from the fractionating process has enough furfural present to make its recovery as furfur-aniline profitable.

^{31a} British Pat. 160,482, Oct. 17, 1919; Chem. Abs. 1921, 2355.

from the separated liquid and the resin which has formed is isolated. Glaessen states the product may be used as a substitute for various natural resins, pitch, asphalt and in making size.

Furfural Compositions.

Inking roller compositions are made by Soane³³ from gluc and glycerine treated with furfural or furfuramide. Gelatine likewise may be treated with a pentose such as arabinose or xylose to produce furfural *in situ*. Glue, glycerine, arabinose syrup and a filler are mixed, the composition is run into molds and heated until it becomes resistant to heat.³³

Schlisky³⁴ has prepared a drying oil by heating furfural with metal compounds capable of yielding oxygen, such as lead oxides, manganese oxide, zinc oxide, or per acids, e.g., furfural is boiled with lead oxide for 6 hours under a reflux condenser.

Furfural and Nitrous Acid.

Furfural combines with chloral-ammonia.³⁵ It reacts very violently with nitrous acid. When an ethereal solution is evaporated a very violent reaction finally ensues with the formation of resinous products.³⁵

Polymerized Thiofurfural.

Cahours³⁷ describes a compound obtained by the action of hydrogen sulphide on furfuramide. When the reaction takes place at a low temperature a white crystalline powder is obtained but in hot concentrated solutions of furfuramide hydrogen sulphide produces a resinous body. Ammonium sulphide acting on furfural also produces the thio compound. Baumann and Fromm³⁸ obtained polymerized thiofurfural by passing dry hydrogen sulphide into an alcoholic solution of furfural. After several hours the milky liquid gradually separates a slightly reddish resinous mass. This product contains some impurity having a strong odor. The resin was found to gradually harden on standing in a desiccator. It is soluble in alkalis and in benzol. Baumann and Fromm obtained a molecular weight of about 2000 indicative of the combination of approximately 20 molecules of the sulphur-containing furfural.³⁹

³³ British Pat. to Usher-Walker, Ltd., and C. E. Soane, 2167, Feb. 10, 1915; Chem. Abs. 1916, 2032.

³⁴ British Pat. 169,003, June 14, 1920.

³⁵ German Pat. 348,087, July 1, 1917; J. S. C. I. 1922, 41, 382A.

³⁶ Schiff and Tassinari, Ber. 1877, 773, 1787; Ann. 201, 356.

³⁷ Wurtz Dict. de chim. Suppl., Part I, 845.

³⁸ Ann. Chem. 69, 85.

³⁹ Ber. 1891, 24, 3591.

⁴⁰ Furfural in alcoholic solution cooled to -5° C., acidified with hydrochloric acid and submitted to the prolonged action of a current of hydrogen sulphide yields a crystalline precipitate of two species of trithiofurfural. One melts at 229° and the other at 128° and is quite readily transformed into the species of higher melting point. By the action of ammonium hydrate in absolute alcohol on furfural another polymer is obtained melting at 90° C., which is insoluble in alcohol. On heating it is decomposed into products similar to the preceding. Wurtz Dict. de chim., 2nd Suppl., Vol. 4, 394; Baumann and Fromm, Ber. 24, 3591; Bull. Soc. Chim. 8, 950.

Chapter 12.

Ketone Resins.

Ketones and Aldehydes.

A considerable range of resinous species has accrued through investigations on the condensation of ketones with themselves or with aldehydes, formaldehyde being the most active agent of its kind in effecting these resin-yielding condensations. Owing to their water-resisting qualities, hardness and toughness, the resins obtained from cyclohexanone and related cyclic ketones are of especial interest. Resins derived from that class of bodies of extraordinarily reactive properties—the ketenes—find mention in this chapter. Should cheap methods of manufacturing ketenes be developed, these substances could scarcely fail of utilization, not alone in resin production but in many other ways. Of the resins described in the present chapter, that one most immediately available is yielded by the reaction between acetone and formaldehyde.

Acetone Resins.

A series of resins are obtained by reaction between acetone or other ketones and formaldehyde, which are of quite a different nature from the phenol-formaldehyde resins. An alkali is used as the condensing agent and the resulting products vary very greatly with the character and amount of alkali employed.

Werner's Resin.

About twenty years ago Werner¹ first called attention to acetone resin. He mixed 40 per cent formaldehyde solution with acetone and found no reaction to take place until alkali was added. If the liquids are mixed in an undiluted form, the addition of a small amount of caustic potash quickly causes a violent reaction and an orange-red condensation product separates. When the substances are mixed in 10 per cent aqueous solution, the reaction proceeds much more slowly. The liquid gradually assumes a dark yellow color with greenish fluorescence. After one hour the condensation product commences to separate as a bright orange-yellow powder and at the end of 24 hours the reaction is complete. During the change the alkalinity of the liquid diminishes

¹ Proc. Chem. Soc. 1904, (20) 196; Chem. Centralblatt 1905, I, 221.

to a considerable degree. The washed and dried product forms an orange-yellow amorphous powder of satiny lustre and possesses a peculiar odor.

The compound is freely soluble in alcohol, acetone or glacial acetic acid and is precipitated unchanged by water. It dissolves sparingly in benzol, chloroform or ether. The same compound, according to Werner, is produced whether acetone or formaldehyde be used in excess.

The addition of hydrochloric acid to the alkaline filtrate resulting from the reaction, produces a yellow precipitate. An analysis by Werner showed the resin and the yellow precipitate from the filtrate to have the empirical formula C_4H_6O . This composition suggests a polymer of $CH:CH.CO.CH_2$. Werner found, however, that the compound behaved as a saturated body, evolving hydrobromic acid on treatment with bromine in glacial acetic acid solutions. A mono-brom compound is formed which, on dilution of the acetic acid solution with water, separates as a red powder.

Müller's Observations.

Müller² also notes that the condensation of acetone with formaldehyde does not give the expected compound methylene acetone. With a small proportion of alkali as a condensing agent keto-butanol $CH_3COCH_2CH_2OH$ is formed. The use of large amounts of alkali, on the other hand, gives rise to an amorphous compound, the constitution of which was investigated by Müller. The results of his elementary analysis are in accord with those obtained by Werner, but molecular weight determinations indicated a di-molecular structure of the formula $C_8H_{10}O_2$. Müller found the resin to be readily attacked in alkaline solution by permanganate affording fatty acids and carbon dioxide. The brom compound $C_8H_8O_2Br_2$ also was prepared. The resin does not exhibit the reactions of a ketone. Neither hydrazones nor oximes could be formed. The resin reacts readily with nitric acid to form a water-soluble nitro compound.

Müller's method of preparing the resin is as follows: 75 grams of 40 per cent formaldehyde solution are mixed with 60 grams of acetone and the mixture is poured into a solution of 50 cc. 30 per cent aqueous caustic soda and 200 cc. 96 per cent alcohol. The reaction mixture is cooled. After standing for 36 hours the reddish-brown reaction mixture is poured into 2 litres of water. 50 to 55 grams of a brown resin are obtained. The moist raw resin possesses an odor of hexenon. This odor is removed by extraction with ether. The resin cannot be crystallized.

Resin Purification.

Purification of the resin was carried out by dissolving 50 grams of the raw resin in 400 cc. hot ethyl alcohol, filtering and adding 100 cc. of methyl alcohol. A solid product separated which was washed and dried. This material possesses no sharp melting point. Carbonization occurs above 300° C. The most highly purified product obtained by Müller was of a light yellow color and had no taste or odor. The color is probably due to a by-product which cannot be eliminated completely.

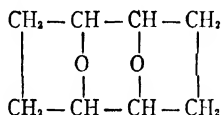
² Ber. 1921, 54, 1142; J. Chem. Soc., 1921, i, 542.

Müller's acetone resin is soluble in ethyl and methyl alcohol, acetone, glacial acetic acid and benzol, less soluble in ether and almost insoluble in ligroin, water and dilute caustic alkali solutions. Intumescence, then carbonization occur when the resin is heated in a test tube. The alcoholic solutions of the resin react entirely neutral.

Müller considers the reactions forming the resin to progress in two stages as follows:

I. $\text{CH}_3\text{CO}\cdot\text{CH}_3 + \text{H}\cdot\text{CHO} \rightarrow \text{H}_2\text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$ and by splitting off water and migration.

II. $2 \text{CH}_2(\text{OH})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3 \xrightarrow{(\text{alkali})}$



Keto-Butanol.

Ketone alcohol or keto-butanol is prepared by Farbenfabriken vorm. Friedr. Bayer & Co., from formaldehyde and acetone by reacting in the presence of a weak alkaline condensing agent. Magnesia, sodium phosphate, borax, and the carbonates of sodium or potassium may be used. Keto-butanol is a liquid boiling at 110°C . On long standing this compound thickens to a viscous syrup. Keto-butanol mixes readily with alcohol or ether but the syrupy product is insoluble.³ Methyl keto-butanol, octodionol and homologues may be prepared by the same procedure.⁴ Claisen and Niegemann,⁵ in 1892, studied the action of formaldehyde on acetone with the expectation of obtaining $\text{CH}_3\text{COCH}:\text{CH}_2$ or $\text{CH}_3\text{COCH}_2\text{CH}_2\text{OH}$. Tollens⁶ has observed that the place of union of formaldehyde with ketones and other aldehydes is adjacent the ketone or aldehyde group. By-product resins of a ketonoid or aldehydic nature are obtained by the action of alkali on pyroligneous acid.⁷

Acetaldehyde and Acetone.

Claisen⁸ observed that alkaline agents such as potassium carbonate and potassium cyanide, caused acetone and acetaldehyde to combine readily even at room temperature to the product, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{COCH}_3$. Claisen gave this the name hydracetyl acetone. This compound, which is a methyl acetonyl carbinol, has a ketonic odor and the consistency of glycol. It mixes with water in all proportions and boils at $77-78^\circ \text{C}$. under a pressure of 19 mm.

Iodo-Resins.

Iodine-containing condensation products of acetone and other ketones with aldehydes have been used by Hertkorn⁹ to replace iodoform as a disinfecting powder. Aliphatic or aromatic compounds may be used separately or in admixture and combination brought about by a condensing agent. Aqueous or alcoholic alkali, carbonates and certain other salts, acids, etc., are mentioned as condensing agents. Polymerized or condensed aldehydes or ketones, oxyaldehydes and ketonic alcohols may be used. Hertkorn mentions trioxymethylene,

³Merling and Köhler, U. S. Pat. 981,668, Jan. 17, 1911; 989,993, Apr. 18, 1911.

⁴Chem. Centralblatt 1910, II, 347 and 1421; German Pats. 223,207 and 227,177, 1910; U. S. Pats. 981,669, Jan. 17, 1911; 991,734, May 9, 1911; 991,735, May 9, 1911.

⁵Ber. 1892, 25, 3164.

⁶Marle and Tollens, Ber. 1903, 36, 1341.

⁷See process of Chute described in Chapter 14.

⁸Ber. 1892, 25, 3164.

⁹U. S. Pat. 901,709, Oct. 20, 1908.

paraldehyde, metaldehyde, croton aldehyde, chloral, salicyl aldehyde, cinnamic aldehyde, mesityl oxide, phorone, chlor acetone, anthraquinone, benzoyl carbinol. These condensation products are either colorless or of a yellowish to deep orange color, according to the condensing agent and the manner of using it.

Hertkorn's Procedure.

A recommended procedure is the following: 100 grams of acetone and 250 grams of formaldehyde are mixed in one-half to two liters of water. 30 to 60 grams of soda lye are added and the mixture is gently heated until spontaneous reaction sets in and the liquid assumes a yellow color. The liquid is cooled and allowed to stand for one or two days with frequent agitation. An orange yellow flocculent precipitate is formed. Heating to a temperature of 40-50° C. at this stage favors the deposition of the orange powder. When the temperature is raised compact orange red masses may appear, which do not soften when the temperature is raised still higher. The precipitate is pulverized and washed. The finely-powdered material is subsequently treated with iodine to yield the iodo product desired. Alcoholic soda may be used instead of soda lye. If the compact masses above mentioned are treated with iodine the addition product is of a horny and compact nature. The iodized product of condensation of acetone and formaldehyde is almost entirely insoluble in water, fairly soluble in alcohol, ether and amyl acetate and very soluble in acetone and other ketones; the solution being of a yellow color. The product is almost insoluble in cold benzine, benzol or oil of turpentine, but is partially soluble in hot benzine and benzol, the resulting liquid being of a reddish color. Condensation products of acetone with croton aldehyde and also with benzaldehyde, of benzyldene acetone with benzaldehyde, of phorone and mesityl oxide with formaldehyde and of acetone with salicyl aldehyde are also mentioned.

Use of a Filler.

A plastic composition has been proposed by Plauson¹⁰ intended for molding to a product resembling wood. It is made from acetone resin and a filling material by precipitation of the resin in the presence of the filler. The latter may be ground wood, peat, straw and various mineral powders. 100 parts of the filler are mixed in a drum with 58 parts of acetone and 100 parts of 30 per cent formaldehyde. Ammonia gas then is introduced into the drum with continual agitation under a pressure of 1 to 3 atmospheres. Reaction is stated to take place and to be complete in 10 to 15 minutes. The excess of ammonia is removed and the water evaporated in vacuo. Another composition is made from 30 parts acetone-soluble rubber resin dissolved in acetone, 60 parts of acetone and 100 parts of 40 per cent formaldehyde. This mixture is incorporated in a mixing drum with 150 to 250 parts of wood meal and there is added a 10 per cent alcoholic or aqueous solution of caustic soda. The reaction is stated to be complete in a half hour without resorting to pressure. The alkali and excess of acetone are removed by washing and evaporation. The amount of caustic soda required is not stated, the strength only of the solution being indicated. From the author's experience with acetone resin this information is required in order to obtain suitable resinous material.

The dry powder is stated by Plauson to be capable of molding into articles at a pressure of 150-500 atmospheres and at a temperature

¹⁰ U. S. Pat. 1,397,144, Nov. 15, 1921; German Pat. 337,960, Jan. 6, 1922.

between 120-200° C. Articles are thus obtained which are said to be inert to alkalis, acids and almost all organic solvents, to possess high insulating properties and to machine satisfactorily. At a pressure of 200-250 atmospheres it is stated the molded article more nearly resembles natural wood. Plauson states that various substances may be added such as shellac, cellulose esters, oils and waxes and acetone-soluble phenol condensation products. He also states that other alkaline condensing agents, namely, alkali carbonates or alkali sulphides, may be employed. The author's experience with acetone resin would indicate none of these alkalis, with the exception of caustic soda or caustic potash, is particularly effective in producing a resin in any way approaching commercial requirements. Plauson states that hexamethylenetetramine may be used in place of formaldehyde. Acetaldehyde may be used but it is more difficult to obtain a resin than when using formaldehyde. In fact Plauson states that the pressure in this case should be from 3 to 10 atmospheres. Methyl ethyl ketone which he states may be used in place of acetone, while capable of forming a resin, at the same time is partially converted into a volatile compound immiscible with water. An aromatic ketone such as benzophenone does not resinify readily with formaldehyde and an alkaline condensing agent. The reaction product of phenyl methyl ketone, phenol and hexamethylene has been employed as a binder in making plastic substances.^{10a} Concerning resins obtained by condensation of acetone with furfural see Chapter II.

Acetone Resin.

This resin for use in molding compositions has been prepared experimentally in the author's laboratory. The method employed yields a product soluble in alcohol and capable of being heated for prolonged periods without reacting further to an infusible, insoluble resinoid. On addition of a catalytic agent to this initial product a highly reactive resin results which, according to the procedure employed, can be made to harden spontaneously or on very short heating in a hot press.

The initial fusible resin is prepared by heating, in a steam jacketed digester, 100 pounds acetone, 250 pounds 40 per cent formaldehyde, and 25 pounds sodium carbonate. The temperature is maintained at 50-60° C. (122-140° F.) for the first part of the reaction, and, due to the self-heating or exothermic nature of the reaction, it is often necessary to cool by circulating water through the jacket of the digester. After the initial exothermic reaction has taken place the temperature is raised to 90-110° C. (194-230° F.) and maintained until a soft yellow resin is precipitated. This requires several hours heating. The resin is drawn off and usually washed with hot water to remove water soluble matter, after which it is dried. Addition of a catalytic agent can be made to an alcohol or acetone solution of the resin or by mixing on heated differential rolls.

^{10a} J. S. C. I. 1915, 623; British Pat. 9292, 1914.

A white insoluble resin described by Plauson,¹¹ which is prepared by mixing 1 mol. of a ketone and 6 mols. of formaldehyde in aqueous solution, or the equivalent amount of one of its polymers, e.g., paraformaldehyde, or of one of its condensation products, e.g., hexamethylenetetramine, is condensed in the presence of alkalis. Acetone and formaldehyde in this way yield a white powder, $C_6H_{12}O_6$, which is tasteless, odorless, infusible, insoluble in organic solvents, and unattacked by acids and alkalis. It is also difficultly combustible, and is a good electrical insulator.

Methyl Ethyl Ketone.

Some experiments carried out in the author's laboratory directed to the resinification of methyl ethyl ketone by formaldehyde will serve to illustrate the properties of this resin. Methyl ethyl ketone one kilo, aqueous formaldehyde, 37 per cent, $2\frac{1}{2}$ kilos and 25 grams of potassium carbonate, dissolved in a small amount of water, were mixed and agitated in a flask placed in a water bath maintained at a temperature of $30-40^\circ$ C. for $2\frac{1}{2}$ hours, after which the temperature was raised to between $50-60^\circ$ for $1\frac{1}{2}$ hours. On standing for a time a layer of a light yellow liquid collected at the top, this liquid being volatile and having somewhat the odor of a light petroleum hydrocarbon. No formaldehyde was detected in the mixture. The aqueous solution beneath the light yellow liquid was of a deep orange color. 500 grams of this liquid were neutralized with dilute hydrochloric acid and dried in a vacuum pan, the gauge registering $27\frac{1}{2}$ inches vacuum during the drying, the temperature ranging up to 63° C. On opening the drier a very strong odor of formaldehyde was noticed and a dark yellow honey-like product amounting to 140 grams was obtained. This product was found to be soluble in water, alcohol, acetone and glycerol, partly soluble in ether and insoluble in benzol. The upper layer of immiscible liquid referred to above was found to be insoluble in water, fairly soluble in benzol and soluble in alcohol and acetone. A distillation (50 gms.) gave the following results:

63° C. to 73° C.	5.5 gms.
73° C. to 83° C.	21.4 "
83° C. to 92° C.	9.8 "
93° C. to 103° C.	4.7 "
103° C. to 113° C.	2.4 "
113° C. to 150° C.	1.9 "

The syrupy or honey-like material was boiled under reflux condenser with 40 per cent aqueous caustic soda. As resinification did not occur immediately, various portions of caustic soda solution were added from time to time over a period of 10 hours, altogether about 12 per cent by weight of this strong caustic soda solution being added. Eventually a yellow soft resin separated. The reaction between methyl ethyl ketone and formaldehyde in the presence of an alkaline vehicle is thus very different from acetone. The latter would have formed a hard resin very quickly under the conditions indicated.

Benzaldehyde and acetone when boiled with caustic soda solution react in part to form a brown resin.

¹¹ German Pat. 351,349, 1920; J. S. C. I. 1922, 41, 720A.

Acetone Mercury Oxide, $2C_3H_6O \cdot 3HgO$.

Acetone is mixed with mercuric chloride and weak caustic potash solution, the filtered liquid is dialyzed and the solution remaining in the dialyzer is precipitated by acetic acid.¹² The substance also is formed by dissolving mercuric oxide in acetone. Solutions gelatinize on heating or standing. When obtained as a precipitate the particles are gelatinous and on drying exhibit a resinous nature.¹³

Methylene Ketone.

A peculiar property of methylene ketone (methylene acetone, methylene-methylethylketone, $CH_3CO.CR:CH_2$) is that of polymerizing to a colorless, hard but elastic mass.¹⁴ Methylene-methylethylketone, boiling point $96^\circ C.$, when held at a temperature of about $30^\circ C.$ for several weeks, polymerized to a hard elastic solid from which billiard balls were formed. These exhibited properties resembling ivory. When treated with concentrated hydrochloric acid the color changes to black without affecting the quality of the polymer in other respects. Suggested uses for the product are glass substitute, lenses and electrical insulation. Lenses made from it have a high index of refraction. Like celluloid, the material softens in hot water and may be molded, coloring agents being added when special colors are required. This same ketone when heated with formic acid to obtain dimethyl octadionol forms a certain amount of polymer appearing as a flexible skin.¹⁵

Miscellaneous Reactions.

Acetone condenses with pyrrole¹⁶ to form an amorphous substance, $C_{22}H_{26}N_4O$. Mineral and organic acids serve as condensing agents but alkalis are ineffective. Resinous bodies also are obtained.¹⁷

Anhydro Enneaheptite, $(C_8H_{16}O_6)$, is a crystalline substance formed by treating acetone (60 grams), 40 per cent aqueous formaldehyde (600 grams), slaked lime (65 grams), and water (6000 grams). Acetone, formaldehyde, and milk of lime, on standing, form anhydroenneaheptite.¹⁸ Xylitone or xylitol¹⁹ easily forms resins on treatment with strong acids. Mesityl oxide, when treated with phosphorus pentachloride, yields an oily non-volatile chloride $C_9H_{10}Cl_2$, the odor of which resembles turpentine. On exposure to the air the compound resinifies.²⁰ Claisen²¹ observed the formation of large amounts of a brown resin on treating acetone with gaseous hydrochloric acid. According to Herzog and Kreidl, the resin results from the polymerization of the mesityl oxide and

¹² Reynolds, Z. Chem. 1871, 254.

¹³ Kutscherow, Ber. 17, 20.

¹⁴ Farbenfabriken vorm. Friedr. Bayer & Co. German Pat. 309,224, Dec. 11, 1917; note also German Pat. 222,551.

¹⁵ Bayer, German Pat. 227,177, Sept. 1, 1909; for preparation of methylene methyl ethyl ketone see U. S. Pat. 981,669, Jan. 17, 1911.

¹⁶ Baeyer, Ber. 19, 2184.

¹⁷ Chelintzev and Tronov J. Russ. Phys. Chem. Soc. 1916, 48, 105 and 748; Chem. Abs. 1917, 452.

¹⁸ Apel, Tollens, Annalen 289, 46; Beilstein, 4th Ed., Vol. I, 642; note Manich and Brose, Ber. 1922, 55, 3155.

¹⁹ Beilstein, 3rd Ed., Vol. I, 1013.

²⁰ Beilstein, 3rd Ed., Vol. I, 1008.

²¹ Ann. 1876, 180, 4.

A white insoluble resin described by Plauson,¹¹ which is prepared by mixing 1 mol. of a ketone and 6 mols. of formaldehyde in aqueous solution, or the equivalent amount of one of its polymers, e.g., paraformaldehyde, or of one of its condensation products, e.g., hexamethylenetetramine, is condensed in the presence of alkalis. Acetone and formaldehyde in this way yield a white powder, $C_6H_{12}O_6$, which is tasteless, odorless, infusible, insoluble in organic solvents, and unattacked by acids and alkalis. It is also difficultly combustible, and is a good electrical insulator.

Methyl Ethyl Ketone.

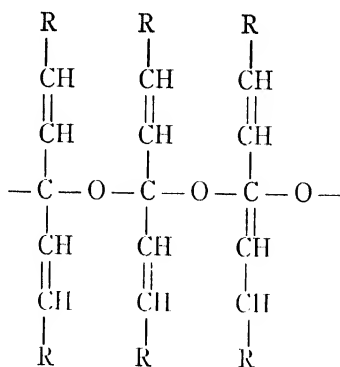
Some experiments carried out in the author's laboratory directed to the resinification of methyl ethyl ketone by formaldehyde will serve to illustrate the properties of this resin. Methyl ethyl ketone one kilo, aqueous formaldehyde, 37 per cent, $2\frac{1}{2}$ kilos and 25 grams of potassium carbonate, dissolved in a small amount of water, were mixed and agitated in a flask placed in a water bath maintained at a temperature of $30-40^\circ$ C. for $2\frac{1}{2}$ hours, after which the temperature was raised to between $50-60^\circ$ for $1\frac{1}{2}$ hours. On standing for a time a layer of a light yellow liquid collected at the top, this liquid being volatile and having somewhat the odor of a light petroleum hydrocarbon. No formaldehyde was detected in the mixture. The aqueous solution beneath the light yellow liquid was of a deep orange color. 500 grams of this liquid were neutralized with dilute hydrochloric acid and dried in a vacuum pan, the gauge registering $27\frac{1}{2}$ inches vacuum during the drying, the temperature ranging up to 63° C. On opening the drier a very strong odor of formaldehyde was noticed and a dark yellow honey-like product amounting to 140 grams was obtained. This product was found to be soluble in water, alcohol, acetone and glycerol, partly soluble in ether and insoluble in benzol. The upper layer of immiscible liquid referred to above was found to be insoluble in water, fairly soluble in benzol and soluble in alcohol and acetone. A distillation (50 gms.) gave the following results:

63° C. to 73° C.	5.5 gms.
73° C. to 83° C.	21.4 "
83° C. to 92° C.	9.8 "
93° C. to 103° C.	4.7 "
103° C. to 113° C.	2.4 "
113° C. to 150° C.	1.9 "

The syrupy or honey-like material was boiled under reflux condenser with 40 per cent aqueous caustic soda. As resinification did not occur immediately, various portions of caustic soda solution were added from time to time over a period of 10 hours, altogether about 12 per cent by weight of this strong caustic soda solution being added. Eventually a yellow soft resin separated. The reaction between methyl ethyl ketone and formaldehyde in the presence of an alkaline vehicle is thus very different from acetone. The latter would have formed a hard resin very quickly under the conditions indicated.

Benzaldehyde and acetone when boiled with caustic soda solution react in part to form a brown resin.

¹¹ German Pat. 351,349, 1920; J. S. C. I. 1922, 41, 720A.

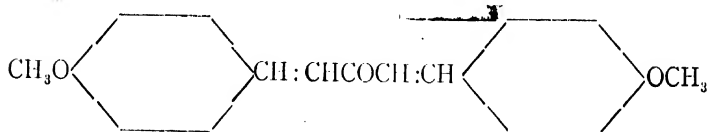


Most of the resins obtained are soluble in benzol, chloroform and various other solvents.

Action of Heat on Dibenzylidene Acetone.

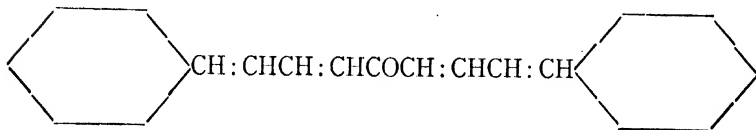
The resinification of this substance was effected by heating in a flask for 9 hours in a stream of carbon dioxide. The temperature with the thermometer in the melt, was 180° C. A slight amount of benzaldehyde was formed. The resin was reddish brown, melting point 85-95° C. It was soluble in benzol, chloroform, ether, tetrahydronaphthalene, acetone, ethyl acetate and glacial acetic acid. The resin was moderately soluble in turpentine and fatty oils but insoluble in alcohol and petroleum ether. Lacquers made from the resin in volatile solvents were of good quality. Efforts to produce the resin by heating the ketone in a solvent boiling at a high temperature (e.g. decahydronaphthalene, b.p. 185-195° C.) did not give satisfactory results.

Dianisylidene acetone



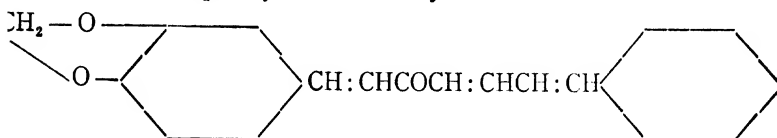
This compound (m.p. 130-131° C.) was heated at 220-225° C. in a stream of carbon dioxide and in 6 hours was almost entirely converted to a reddish brown brittle resin, softening at 70° C. and molten at 100° C.

Dicinnamylidene acetone.



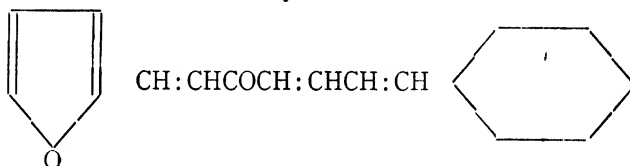
Heating this compound causes a very sudden resinification. At 180° C. the thermometer suddenly rises about 100° and within a few seconds a reddish brown brittle resin forms. The melting point of the original material is 142° C., that of the resulting resin 130-145° C. The resin is soluble in benzol and acetone but is sparingly soluble in ether.

Piperonylidene cinnamylidene acetone.



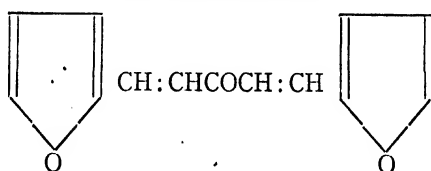
When this compound was gradually heated to 210° C. in carbon dioxide, a marked exothermic reaction occurred and in the course of a few minutes a reddish brown brittle resin (M.P. 125-135° C.) formed.

Furfuralcinnamylidene acetone.



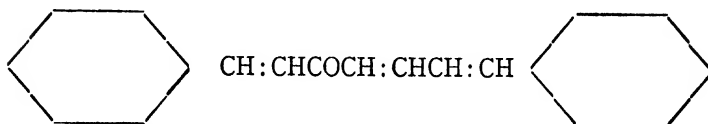
M.P. 96-98° C. This compound likewise resinifies with strong evolution of heat. When heated gradually to 190-200° C. the temperature suddenly rises to about 300° C. and the resulting resin melts at 135-155° C.

Difurfural acetone.

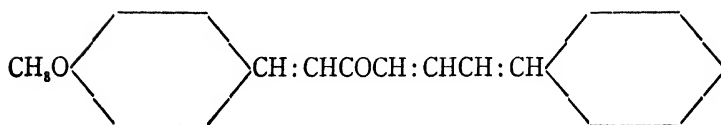


A brittle resin, melting between 55 and 75° C. is obtained on heating 5 hours at 200-210° C.

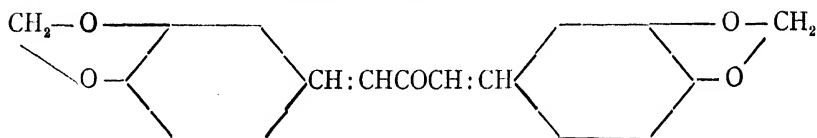
Benzylidene cinnamylidene acetone.



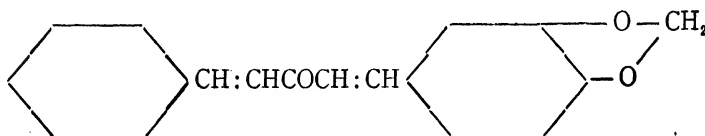
M.P. 109-110° C. Resinification occurs on heating for a few minutes at 220° C. The resin has a melting point of 115-120° C.

Anisylidene cinnamylidene acetone.

M.P. 138° C. Heating for a short time at 220° C. resulted in a brown resin, M.P. 135-140° C.

Dipiperonylidene acetone.

M.P. 185° C. Heating in carbon dioxide at 260° C. for a short time yielded a dark brown brittle resin of melting point 155-170° C.

Benzylidene piperonylidene acetone.

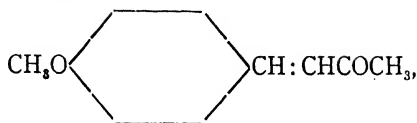
A reddish brown resin was obtained by heating for 5 hours in carbon dioxide at 200° C. The resin melted at 70-80° C. and possessed a glassy fracture.

Further work by Herzog and Kreidl³⁰ confirmed their view that the unsaturated ketone grouping constituted a resinophore effective in the formation of resins by exposure to heat. Benzylidene acetone, $C_6H_5CH:CHCOCH_3$, heated for 12 hours at 230-240° C. in a current of carbon dioxide yielded a reddish brown moderately hard resin of melting point 60-65° C. This was soluble in benzol, chloroform and various other volatile solvents, also in fatty oils. It was very slightly soluble in petroleum ether and alcohol. Solutions yielded a rather stable varnish coating. It may be noted that Borsche called attention to the resinification of benzylidene acetone (benzal acetone) on contact with sodium ethylate. The product was practically insoluble in all common solvents. This insolubility is indicative of an advanced stage of resinification.^{30a}

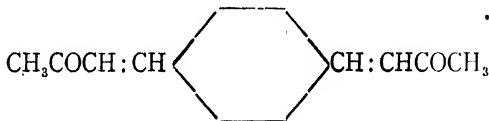
³⁰ Z. angew. Chem. 1922, 35, 641.

^{30a} Ber. 1909, 42, 4496.

Anisylidene acetone,

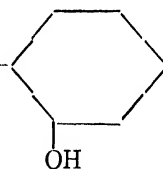


when heated for 4 hours at 220-225° C. in a current of carbon dioxide yielded a brittle transparent resin which Herzog and Kreidl found soluble in various organic solvents. Vanillal acetone likewise gave a brittle resin on heating to 230° C. This resin was soluble in a dilute solution of caustic alkali. On acidification the resin was precipitated as an amorphous powder. Cinnamylidene acetone, $\text{C}_6\text{H}_5\text{CH} \text{:} \text{CHCH} \text{:} \text{CHCOCH}_3$, at 220° C. yielded a brittle transparent resin. Cinnamylidene acetophenone, $\text{C}_6\text{H}_5\text{CH} \text{:} \text{CHCH} \text{:} \text{CHCOC}_6\text{H}_5$, at 190-200° C. resinified to a product melting at 58-64° C. Terephthalaldehyde and acetone condensation product,



containing two unsaturated ketone resinophore groups of the character previously described was heated for an hour in a current of carbon dioxide at 210°. This treatment served to produce a reddish brown brittle resin melting between 129-133° C. Freudenberg and

Orthner³¹ found that oxychalkon, $\text{C}_6\text{H}_5\text{CH} \text{:} \text{CHCO}$ —



(benzal-*o*-oxyacetophenone) resinifies partially on treatment with dilute hydrochloric acid.

Phenyl Vinyl Ketone.

Various bases and acids, e.g., caustic soda, calcium and barium oxides, hydrochloric acid, were tried by Marle and Tollens³² as catalysts in reacting on acetophenone with formaldehyde. Resins and a clear syrupy product were obtained in most cases but with ammonium chloride a crystalline substance, tri-methylol-bis-acetophenone was isolated. When this product was distilled with steam, an oil, phenyl vinyl ketone, was collected. The oil solidified in the course of a few days

³¹ Ber. 1922, 55, 1748.

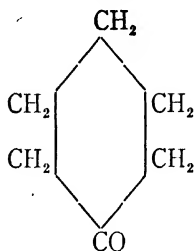
³² Ber. 1903, 36, 1351.

to a horny mass, so hard that a hammer was required to pulverize it. The hard material is polymerized phenyl vinyl ketone.

During the operation of making ionone by the condensation of citral with acetone, a portion of the material polymerizes to a soft and sticky resin.

Cyclic Ketone Resins.

Cyclohexanone



Monocyclic ketones resinify when heated with alkaline condensing agents for a protracted period so that the reaction proceeds beyond the stage of formation of simple condensation products. 200 parts of cyclohexanone heated with 100 parts of alcoholic potash (2 parts methyl alcohol to 1 part potassium hydrate) under pressure at 200-220° C. for 20 hours afford a resin. The conversion is complete. The resin is soluble in alcohol, benzol, cyclohexanone and in linseed oil.⁸³ Solid potassium hydrate also may be used as a condensing agent. 100 parts cyclohexanone with 80 parts of a 25 per cent solution of sodium hydrate in methyl alcohol, heated under a reflux condenser for 48 hours, react to a resinous mass.

Methyl cyclohexanone.

20 parts of the para compound, heated with 10 parts of alcoholic potash (methyl alcohol) for 20 hours at 200-220° C. also yield a resin. This is boiled with dilute hydrochloric acid and dried. A white powder is obtained which is soluble in benzol, cyclohexanone and linseed oil.

Cyclohexylidene cyclohexanone.

Alcoholic potash resinifies this compound when boiled together under a reflux condenser for 24 hours. An almost colorless resin, soluble in alcohol and linseed oil, results.

Acid Condensation.

Mineral acids, e.g., 50 per cent sulphuric acid or alcoholic sulphuric acid and zinc chloride (with or without additions of hydrochloric acid) act as condensing agents on monocyclic ketones converting them to

⁸³ Badische, German Pat. 337,993, June 14, 1919; J. S. C. I. 1921, 631A; British Pat. 146,498, July 5, 1920.

resins.³⁴ The products are difficultly soluble in alcohol but soluble in benzol and in linseed oil. Cyclohexanone forms a useful resin by such condensation. Ruhemann³⁵ found a cyclohexanone derivative, $C_{26}H_{28}O_6$, to be converted to a resin on boiling with potassium hydroxide. Hydrochloric acid at 120° C. also yields a resin. Phenylhydrazine reacts with the hexanone derivative yielding an oil. The addition of acetic acid precipitates an amorphous solid which cannot be crystallized.

Herzog and Kreidl³⁶ determined the action of heat on a number of cyclic ketones. Benzylidene alpha tetralon was heated for 20 hours at 270-280° C. yielding a brittle resin melting between 75-90° C. Cinnamylidene alpha tetralon resinified on exposure for a few minutes to a temperature of about 230° C.

Cyclohexanone and Formaldehyde.

Resins possessing attractive properties are made by reacting on cyclohexanone with formaldehyde in the presence of an alkaline or acid catalyst. Equal molecular proportions of the hexanone and formaldehyde are appropriate for forming resins. A large proportion of formaldehyde tends to yield products affected by water. To make this type of resin³⁷ 100 parts by volume of cyclohexanone are heated to 85-90° C. under a reflux condenser, 3 volumes of aqueous caustic soda solution of 50° B. are added and 110-120 volumes of 30 per cent formaldehyde solution are introduced in small portions, with stirring. At the close of the reaction, a heavy oil settles. At 50-60° C. the aqueous liquor is decanted and the soft resin kneaded in water until free from alkali. An opaque mass is obtained which is heated to 110-120° C. to remove water and is then further heated at 130-135° C. until a sample on cooling sets to a hard, transparent resinous body. In this manner a very soluble product is obtained, dissolving readily in alcohol, ether, acetone, chloroform, amyl acetate, benzol, toluol and cyclohexanone. Commercial cyclohexanone possesses an unpleasant odor but the resin is practically odorless. As prepared by the author, the color is reddish when caustic alkali is employed to bring about the reaction. With milder alkalis and anhydrous formaldehyde (paraform) a colorless resin has been obtained in the author's laboratory. Infusible products result from protracted heating of the cyclohexanone resin. This resin is one of the more promising types of synthetic products. It can be given a considerable degree of hardness, yet remain soluble in a great variety of organic solvents. The raw material, cyclohexanone, is derived from phenol by a process involving hydrogenation of the latter.

According to the Badische Co., methyl cyclohexanone likewise yields a resin and sulphuric acid can replace caustic alkali as a catalyst.

³⁴ Badische, British Pat. 170,351, July 13, 1920; J. S. C. I. 1922, 41, 23A.

³⁵ J. Chem. Soc. Trans. 1909, 95, 109.

³⁶ Z. angew. Chem. 1922, 35, 641.

³⁷ Badische, German Pat. 339,107, June 1, 1918.

Acetaldehyde and Cyclohexanone.

From cyclohexanone and acetaldehyde a resin is formed which has promising applications in the preparation of varnishes and electrical insulation. The resin may be made by heating to 80-90° C., cyclohexanone 100 parts, alcohol 100 parts, and caustic soda 1 part in 50 per cent solution and adding a 25 per cent solution of acetaldehyde 250 parts. The alcohol is distilled off and the resulting oil washed and allowed to solidify.³⁸

Acetophenone.

The action of formaldehyde on acetophenone, in the presence of acid or alkaline reagents, calcium, barium or sodium hydrate or hydrochloric acid, is to form a resin and a non-crystallizable syrup.³⁹

A cyclic diketone obtained by Becker and Thorpe⁴⁰ as a crystalline substance was found to resinify on keeping.

Ketene Resins.**Ketenes, $R_2C:CO$.**

These constitute a group of substances discovered by Staudinger since 1905. They differ markedly from the ketones proper in their great reactivity.⁴¹

The residues, R, may be either aromatic or aliphatic hydrocarbon radicals. All these compounds can be derived from ketene, $CH_2:CO$, a colorless poisonous gas, of disagreeable odor. It is easily polymerised (by metallic chlorides or tertiary bases), yielding a colored resin. The best characterized of these compounds are dimethyl, $(CH_3)_2C:CO$, and diphenyl-ketene, $(C_6H_5)_2C:CO$. Monomethyl, $CH_3.CH:CO$, and monoethyl-ketene, $C_2H_5.CH:CO$, have properties similar to those of carbon suboxide, $O:C:C:C:O$. and resemble the isocyanates in their great reactivity. The disubstituted ketenes are colored and readily oxidize in the air. The monosubstituted ketenes undergo polymerization more readily than the diketenes, giving cyclobutane derivatives which polymerize on heating.

Ketene, $CH_2:CO$.

Metallic chlorides such as zinc or ferric chloride, sodium and potassium and also tertiary organic bases such as pyridine act as polymerizing agents yielding dihydracetic acid and a resin.⁴²

³⁸ Chem. Age, London, 1922, 7, 91; Dreyfus, British Pat. 181,575, 1921; Chem. Met. Eng. 1922, 27, 755.

³⁹ Van Marle and Tollens, Ber. 1903, 36, 1351; see phenyl vinyl ketone, chap. 18.

⁴⁰ J. Chem. Soc. Trans. 1922, 1303.

⁴¹ The history of the ketenes with a table of properties of those already prepared is given by Sommelet (Rev. gén. sci. 1921, 32, 465). Their preparation, physical properties, reaction with heat and chemical properties are given in detail. The article is well illustrated with structural equations and is an excellent review of ketene chemistry.

⁴² Beilstein, 4th Ed., Vol. 1, 724; Staudinger, Klever, Ber. 41, 1516.

In the polymerization of the ketenes, derivatives of cyclobutanol are usually formed, while isocyanates chiefly give derivatives of isocyanuric acid, the double union in the 2,3-position being saturated in both cases. It might be assumed that since $(C_6H_5)_2C:CO$ has a reactive double bond between carbon atoms, it would polymerize easily, while simple ketenes and isocyanates would polymerize with difficulty, but just the opposite is the case, this behavior being explained on the basis of differences in the disposition of partial valences.⁴³

⁴³ Staudinger, *Helvetica Chim. Acta* 1922, 5, 87-103. Resinous products are obtained from ketene acetal or vinylidene glycol diethyl ether. Scheibler and Ziegner, *Ber.* 1922, 55B, 789; *Chem. Abs.* 1922, 16, 3067.

Chapter 13.

Urea and Thiourea Resins.

Urea (carbamide) $\text{CO}(\text{NH}_2)_2$ reacts with formaldehyde to yield amorphous products, which, while not so typically resinous as some of the substances described in this volume, have, nevertheless, certain properties of interest to the investigator in synthetic resins.

These amorphous products can be made very white or glass-like and possess the property of melting and then hardening within a narrow range of temperature. The hardened products are infusible or very resistant to heat. Hence the initial fusible condensation product may be used as a basis of a molding compound which will become rigid under heat and pressure. In this way white molded articles have been made in the author's laboratory which exhibited a glossy surface of a remarkable degree of hardness and which would not readily fuse when exposed to strong heat. When held in a Bunsen flame, there is no indication of definite melting but the article eventually blackens and ignites with difficulty. Methods of producing urea cheaply should lead to the development of white molding compounds of commercial significance. Just what is the nature of the bodies formed by the condensation of urea and formaldehyde is still a subject of discussion among chemists.

Goldschmidt's Amorphous Product.

In studying the reaction products of formaldehyde on the hydrochloric acid salts of amines Goldschmidt¹ investigated the action of formaldehyde on urea hydrochloride. Urea was dissolved in dilute hydrochloric acid and an excess of formaldehyde added. After an hour a thick white granular precipitate separated which was not soluble in any solvent. Strong acids decompose the substance while alkalis are without influence. Analysis indicated the compound $\text{C}_5\text{H}_{10}\text{N}_4\text{O}_3$, thus suggesting that 2 molecules of urea unite with 3 molecules of formaldehyde with the elimination of 2 molecules of water.

Further investigation by Goldschmidt² led him to the following conclusions: If formaldehyde is allowed to act on urea various condensation products are obtained according to whether acid, neutral or alkaline solutions are used. The condensation products obtained are partly insoluble in water and in the common solvents and in part they

¹ Ber. 1896, 2438.

² Chem. Z. 1897, 46, 460 and 586.

attract water easily so that their purification and analysis involve difficulties. In acid solution the body $C_6H_{10}N_4O_3$ is formed. If urea is allowed to stand for 24 hours with an excess of 40 per cent aqueous formaldehyde after the solution has been rendered alkaline there is obtained a white precipitate soluble in hot water and precipitated by alcohol as a jelly. Mineral acids split off formaldehyde as is the case also on long boiling with water. Exposed to the air the body gives off formaldehyde slowly, hence has a disinfecting value. The analysis of the substance showed a fair agreement with the formula $C_3N_2O_3H_8$. In neutral solution Goldschmidt obtained mostly a mixture of a substance which was partly soluble and partly insoluble in water.³

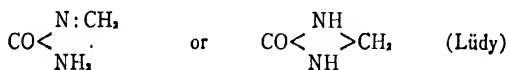
About ten years later Einhorn and Hamburger⁴ investigated the same reaction and cast some doubt on the correctness of Goldschmidt's conclusions.⁵

Following Goldschmidt's method, 1 part urea and 5 parts commercial formaldehyde were reacted in caustic alkali solution for 24 hours. A white amorphous precipitate gradually separated which was insoluble in alcohol, ether and cold water, dissolving in hot water with partial decomposition. However, analyses gave results quite different from those of Goldschmidt's and the conclusion was reached that totally different results were obtained when the alkaline concentration was varied. Goldschmidt's product was supposed, therefore, not to be a pure one and it was assumed by Einhorn and Hamburger that the product he analyzed had merely the accidental composition of dimethylol urea.

Dixon's Investigations.

Dixon⁶ likewise is not in agreement with the conclusions of Goldschmidt. From a slightly acidified solution of urea (1 mol.) the condensation product with 0.75 mol. of formaldehyde is methylene urea. With 1 mol. of formaldehyde it is slightly contaminated with Goldschmidt's compound, $C_6H_{10}O_3N_4$. With $1\frac{1}{2}$ mols. of formaldehyde and thence forward up to well beyond 2 mols, the latter compound is the sole product. Further increase of the formaldehyde ratio diminished

³ Tollens (Berichte 1896, 2751) notes that Goldschmidt overlooked the work of Hölzer (Berichte 1884, 17, 659; 18, 3302, Ann.) and Lüdy (Wien. Akad. Ber. 118, IIb, 191 (1889) obtained from formaldehyde and urea the simple compound $C_4H_4N_2O$.



The various analyses made by Hölzer indicate that perhaps a trace of water is present in this substance. The substance is characterized through its slight solubility in all common solvents.

⁴ Ber. 1908, 41, 24.

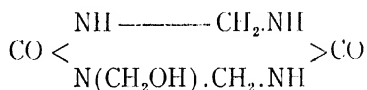
⁵ Chem. Z. 1897, 460; German Pat. 97,164; Friedlander, Fortschritte d. Teerfarbenfabrikat V, 721.

⁶ Trans. Chem. Soc. 1918, 113, 238.

the yield, which at 4 mols. is small, the product being a substance, $C_3H_{12}O_4N_4$. With 11 mols. condensation ceases.

The precipitates obtained from urea in solutions containing variable proportions of formaldehyde, although differing, it may be widely in composition, exhibit a close general resemblance. They occur in minute, white granules, apparently having an amorphous structure, each of which, in plane-polarized light, usually displays a black cross, like that observed in the granules of certain starches.

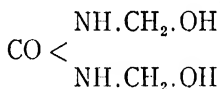
The formula proposed by Goldschmidt for his compound does not appear to be in harmony with its decomposition into urea and formaldehyde by dilute acids. It is slowly attacked by hot alkalies but no methylamine is detected. Dixon therefore considers Goldschmidt's compound to be a methylol derivative



Two compounds, the mono and dimethylol urea, formed by the arrested condensation of urea and formaldehyde are of interest to investigators in the field of synthetic resins. These compounds are always formed when formaldehyde reacts on urea in the presence of alkaline condensing agents, such as carbonated or caustic alkalies, alkaline earths, etc., and may be isolated according to Einhorn and Hamburger, if the condensing agent is removed or neutralized at the right moment. If this is not done, the condensation proceeds further especially as in the case of Goldschmidt when an excess of formaldehyde is not used.

As the dimethylol compound is of special significance it will be first described.

Dimethylol Urea.



Procedure of Einhorn and Hamburger.

To a solution of 0.4 gm. barium hydrate in 26.7 gm. formaldehyde of 37.4 per cent (equivalent to 2 molecules of CH_2O) 10 gms. of urea are added and the temperature is held at 25° or not higher than 30° until the formaldehyde is completely united. This point is determined by Tollen's solution, which, added to a sample of the reaction mixture, does not cause an immediate separation of metal. The reaction takes from 5 to 15 minutes. Carbon dioxide is at once introduced to make the barium hydrate inactive. The liquid is dried in a desiccator without removing barium carbonate and the residue extracted with warm 80 per cent alcohol. By cooling the filtered solution 8 gms. of dimethylol urea separates. 2 gms. more may be obtained by strong cooling of the mother liquor. Dimethylol urea crystallizes from absolute alcohol in small well-formed prisms and from dilute alcohol or water as small shiny plates.

While rather easily soluble in cold water and in ethyl and methyl alcohol on warming, it is insoluble in ether and the other common organic solvents. On heating it begins to sinter at 121°C. and melts at 126° to a clear liquid. At 137 to 138° this changes into an *amorphous* white body which does not melt on further heating but decomposes at 260° without melting. When dimethylol

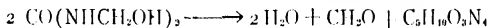
urea is heated in a test-tube the odor of formaldehyde and basic decomposition products is noted.

Dimethylol urea reduces Tollen's solution only after some time. Its not too dilute aqueous solution on the addition of alkali separates slowly a white amorphous precipitate. Dilute mineral acids cause the precipitate to form in several hours.

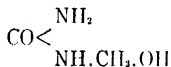
Dimethylol urea was prepared by Dixon⁷ from a neutralized solution of urea (1 mol.) in a little more than 2 mols. of formaldehyde. The reaction mixture was exposed for a day or two in a vacuum desiccator. Dixon observed that the fused material soon began to decompose (m.p. about 123° C.), water and formaldehyde escaping and a white amorphous solid remaining. When heated alongside a pure specimen of the compound $C_5H_{10}O_3N_4$ (Goldschmidt's compound) both decomposed at the same moment with similar effervescence and browning at 255° C. (both samples introduced into the bath at 235° C.)

By condensing an aqueous solution with dilute hydrochloric acid, the same product was obtained as by heating. It gave nitrogen 32.8 per cent, whereas $C_5H_{10}O_3N_4$ requires nitrogen 32.18 per cent.

The end result of these changes may thus be represented



Monomethylol urea. (Einhorn and Hamburger Method.)



6.5 cc. formaldehyde (37.4 per cent) are dropped slowly into an ice-cooled solution of 5 gms. urea and 0.1 gm. barium hydrate in 5 cc. water. Carbon dioxide is introduced immediately. The absence of free formaldehyde is indicated by Tollen's reagent, which condition occurs in a few minutes. The solution is filtered and evaporated in a desiccator affording monomethylol urea as a crystalline mass. Crystallized from alcohol the product melts at 111° C.

Monomethylol urea is easily soluble in cold water. It is also easily soluble in methyl alcohol but insoluble in ether. Unlike dimethylol urea, the addition of dilute mineral acids and also acetic acid produce almost instantly a flocculent amorphous precipitate.

Dixon⁸ considers the procedure recommended by Einhorn and Hamburger for preparing methylol urea to be unnecessarily elaborate. By exposing for a day or two, in an exhausted desiccator, a solution of urea (1 mol.) in formalin (1 mol.) just neutralized by dilute alkali hydroxide, a viscid crystalline paste was obtained by Dixon. From this, after two recrystallizations from alcohol, methylol urea was isolated in brilliant flattened prisms, melting at about 110° C.

The aqueous solution was odorless and gave with sodium nitroprusside and phenyl hydrazine no reaction for formaldehyde. With neutral mercuric nitrate no trace of urea could be detected. On acidification, however, formaldehyde was observed long after the process appeared to be complete.

From a neutral solution of urea (1 mol.) in formalin (1 mol.), Dixon found that methylol urea, together with a little dimethylol urea, is deposited on concentration in a vacuum over sulphuric acid. The former compound, it would seem, is a near precursor of methylene urea; for such a solution, if kept for one and a half hours, so as to give the components a little time to combine before treatment with acid (they do not quickly unite in quantitative amount), began to condense nearly twice as soon as a mixture otherwise similar but freshly prepared. Moreover, when ready-formed methylol urea, in like circumstances of concentrations and of temperature, was acidified to the same extent, condensation started in one-fifteenth of the time required by a freshly-made mixture of urea and formaldehyde. Dimethylol urea, on the other hand, is

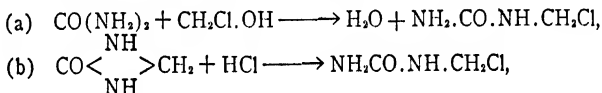
⁷ Trans. Chem. Soc. 1918, 113, 247.

⁸ Trans. Chem. Soc. 1918, 113, 246.

relatively slow to condense—a fact already noted by Einhorn and Hamburger (*loc. cit.*). The reason, no doubt, is that the dimethylol derivative of methylene urea resists formation in the presence of acids; so that, until time enough has passed for the elimination of a certain amount of formaldehyde, condensation is barred. No doubt, too, the complete stoppage of the urea-formaldehyde condensation by a very large excess of formaldehyde is due to the maintenance of the urea in the state of its dimethylol derivative; if the uncondensable mixture is added to a concentrated aqueous solution of urea, a precipitate separates forthwith.*

If urea (1 mol.) is dissolved in formalin (1 mol.) previously saturated with hydrogen chloride (and so changed into chloromethyl alcohol), no precipitate appears, a clear syrup being formed instead. If hydrogen chloride is passed through a molecular solution of urea in formalin until the clot which first separates dissolves again, a clear syrup is formed, as before. Finally, if hydrogen chloride is led over moist, ready-formed methylene urea (or if the latter is added to fuming hydrochloric acid), the solid disappears, giving place to a syrup. Each of these syrups, when poured into water, yields instantly a voluminous, white precipitate of the condensation product. On prolonged exposure in a vacuum over lime and over sulphuric acid, a clear, odorless, resinous material is left; deliquescent, evolving with cold sulphuric acid fumes of hydrogen chloride, and decomposed at once by water, the whole of the contained halogen passing into solution as hydrochloric acid, while a condensation product is deposited.

These changes, perhaps, may be represented by the equations:



the product, with excess of water, decomposing as earlier suggested (in the latter equation, for simplicity, the halved formula is used for methylene urea). The substances, however, were not pure, nor, by reason of their deliquescence and instability, could any method be devised for their purification.

From random acidified mixtures of urea and formaldehyde, Goldschmidt's product, $\text{C}_4\text{H}_{10}\text{O}_2\text{N}_4$, is the product likely to preponderate. The result, however, depends on the conditions imposed; and that different workers, handling these ill-defined amorphous, insoluble and generally similar materials should have disagreed, more or less, as to the outcome, is not surprising.¹⁰

Substituted Ureas.

Herzog¹¹ has studied the effect of heating disubstituted ureas and finds that when such bodies are subjected to a temperature near their melting point resinification will occur on protracted heating due to the

*It is probable "having regard to the above facts, one may reasonably judge that methylene urea results from the decomposition of some compound, generated by the action of, say, hydrochloric acid on methylol urea. Of the stages that must occur, the first is probably the change of $\text{NH}_2\text{CO.NH.CH}_2\text{OH}$ into $\text{NH}_2\text{CO.NH.CH}_2\text{Cl}$, a compound, likely to be unstable, owing to the loss (at least, if water is present) of hydrogen chloride. Through the elimination of hydrogen chloride there originates the residue, NH.CO.NH.CH_2 , when by

polymerization, the compound $\text{CO} < \begin{array}{c} \text{NH.CH}_2\text{NH} \\ \text{NH.CH}_2\text{NH} \end{array} > \text{CO}$ (methylene urea) could

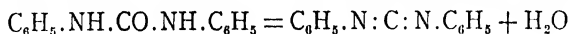
occur."

¹⁰Action of alkalis on urea, see Werner, *Trans. J. Chem. Soc.* 1918, 113, 84 and 604.

¹¹Oester. *Chem. Z.* 1921, 24, 76.

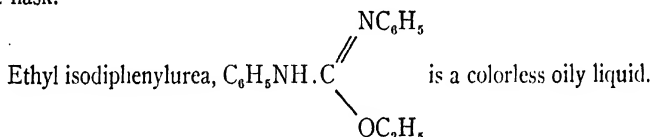
elimination of water and formation of carbo-di-imides. These polymerize to resinous substances.

s-Diphenylurea, melting point 240°C ., was heated in an air bath for about 40 hours to $235\text{--}240^{\circ}\text{C}$. The following reaction progressed:

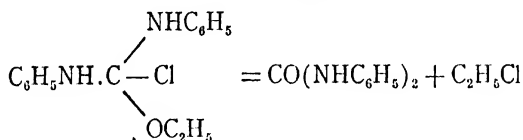


Because of the high temperature at which the reaction took place a considerable amount of decomposition occurred with the formation of aniline. On removal of aniline by vacuum distillation a resin was obtained by Herzog which was identical in its properties with that derived by heating thiocarbamilid.¹²

s-Di ortho tolylurea, $\text{C}:\text{O}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3)_2$, melting point 256°C ., after 24 hours heating at 270° afforded a dark resin having a lustrous surface and exhibiting a satisfactory degree of solubility in benzol. In view of the tendency of the raw material to sublime it was necessary during the heating to return to the heating flask from time to time that portion of the substance which collected as a sublimate in the neck of the flask.



On treatment in petroleum ether with dry hydrochloric acid a salt was obtained which melts between 60 and 80°C ., then solidifies to a compound melting at 235°C . During the change ethyl chloride is evolved.¹³



Urea and Formaldehyde without Condensing Agents.

John¹⁴ recommends condensation of urea and formaldehyde without the presence of a condensing agent, protracted heating being employed to bring about the reaction. In this way he obtains an initial product of condensation which is soluble in water and forms a solution which may be used as an adhesive. Further heating brings about a second stage of condensation affording a solution which will gelatinize on cooling. Colorless transparent elastic masses insoluble in water and alcoholic solvents are thus obtained. John claims this product can be used as a substitute for india rubber.

¹² For a more complete consideration of this phase of resinification see following discussion on thiourea.

¹³ Lengfeld and Stieglitz, Ber. 1894, 27, 926.

¹⁴ U. S. Pat. 1,355,834, Oct. 19, 1920; British Pat. 151,016, Sept. 14, 1920; J. S. C. I. 1922, 47, 183A; Chem. Abs. 1921, 15, 418.

The condensation product can be hardened by exposure to a temperature of about 80° C. The directions by John for furnishing the water-soluble substance are not well detailed. He states five parts of 40 per cent aqueous formaldehyde and one part of urea are heated in a distilling vessel until an adequate proportion of the liquid is distilled when an adhesive solution is obtained. Six parts of aqueous formaldehyde and one part of urea are distilled until about half the liquid has been expelled. On cooling the gelatinous product referred to above is obtained. Thiourea, acetyl urea and benzoyl urea may be used in substitution for ordinary urea (carbamid). In addition to the proposed use of the product as a substitute for rubber and ebonite John suggests its application as a lacquer or impregnating material and as a substitute for celluloid.

Alkaline Catalysts.

Pollak¹⁵ obtains condensation products by heating urea, thiourea, or their derivatives with formaldehyde or a polymer in the presence of a base, such as ammonia, hexamethylenetetramine, pyridine, or urea itself. The initial condensation product first produced is a colorless liquid, soluble in water; on further heating, this is transformed into an intermediate rubber-like product, which is insoluble in water and infusible; the final product, obtained by still further heating or by combined heat and pressure, is a hard infusible transparent mass, insoluble in acids and alkalis. The presence of free formaldehyde is preferably avoided during the conversion of the initial product into the intermediate and final products; that is to say, the formaldehyde should not be present in greater excess than corresponds to 3 molecules of formaldehyde to 1 mol. of urea. Filling substances may be added before the hardening treatment, e.g., wood-pulp, asbestos fibre, chalk, plaster of Paris, carborundum, or sand; or a solution of the initial product, or the initial product itself, may be used for impregnating wood, paper, pasteboard, or asbestos fabric. Steam packings and piston-rings may also be impregnated with a solution of the initial product, hardening being effected by the heat of the steam. Tubular bodies may be prepared by winding a band of impregnated paper or fabric into a heated drum.

Pollak¹⁶ calls attention to the effect of certain salts of weak acids on the initial water-soluble condensation products from aldehydes and urea or thiourea. Hardening may be prevented or retarded by adding salts of weak acids, such as alkali or alkaline earth salts of organic carboxylic acids or weak organic acids. Hardening may be accelerated by adding salts of strong acids such as sulphates, chlorates, chlorides or nitrates, also ammonium sulphocyanate and other ammonium salts. Hardening takes place in any case when the condensation product is

¹⁵ Chem. Abs. 1922, 995; British Pat. 171,094, Nov. 1, 1921; note also Chem. Abs. 1921, 1387.

¹⁶ Chem. Age, London, 1922, 7, 214; British Pat. 181,014, 1921.

subjected to heat treatment. In an example, a condensation product formed from urea, formaldehyde, and hexamethylene tetramine may be rendered permanently liquid by the addition of sodium acetate or borax. A transparent solid may be produced by adding ammonium sulphocyanate, potassium sulphate, nitrate, chloride, chlorate, iodide, or sulphocyanate, or by evaporating in vacuo.

Aqueous solutions of the condensation products obtained by the action of formaldehyde on urea or its derivatives, including thiourea, with or without addition of borax, are used by Pollak¹⁷ as stiffening agents for hats or paper; e.g., the material is impregnated with a 5 to 10 per cent solution of the condensation product, and, after exposure for fifteen minutes to dry steam to remove excess of water and formaldehyde, is ironed. Photographs may be stiffened and given a water-proof coating by moistening them with an 8 per cent solution of the condensation product, and then passing them between hot rollers. These solutions give transparent colorless coatings, but coloring agents may be added if desired.

Acid Catalysts.

Turbid masses resembling meerschaum and porcelain have been produced by Goldschmidt and Neuss^{17a} from urea and formaldehyde in the presence of at least 3 per cent of acid. Not more than 1.2 parts of formaldehyde is used to 1 part of urea. Proportions employed are calculated on the anhydrous substances. The urea is dissolved in the formaldehyde solution, heat applied and nitric, sulphuric or hydrochloric acid added. Finally, the mixture is poured into molds.

Thiourea Resins.

A class of resins of a more complicated character are those containing the grouping —N:C:N— and generally derived from thioureas (thiocarbamide). Although carbo-di-imides, they are more conveniently termed thiourea resins.¹⁸

About 1874 Weith^{18a} found carbo-diphenylimide $\text{C}(\text{NC}_6\text{H}_5)_2$ to exist in two modifications, one melting at $160\text{--}170^\circ$ and the other being a viscous liquid at room temperature. The nature of these imide bodies has been the subject of much study and some controversy. Huhn^{18b} found phenyl-p-tolyl thiourea to be readily desulphured on heating in benzol with mercury oxide. Carbo phenyl-p-tolylimide formed.

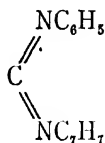
¹⁷ British Pat. 157,416, 1921; J. S. C. I. 1922, 41, 459A.

^{17a} Chem. Met. Eng. 1923, 82; British Pat. 187,605, 1922.

¹⁸ Process of making thioureas see J. S. C. I. 1922, 41, 197A; British Pat. 164,326, 1921, Goodyear Tire and Rubber Co.

^{18a} Ber. 7, 10 and 1306; 9, 810.

^{18b} Ber. 1886, 19, 2404.

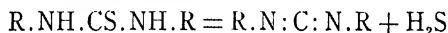


The freshly distilled product is a liquid which becomes viscous on standing and eventually changes to a brittle "glass-like" mass. The change is due to polymerization.

The carbo-phenyl-o-tolylimide is a viscous liquid likewise polymerizing to a brittle product. This was observed by Huhn to change gradually in a few weeks' time to a mass resembling porcelain. A brittle solid also was obtained in preparing α carbo-dinaphthylimide.¹⁰

Resinophore Group — N : C : N.

These investigators were studying carbo-di-imides for other reasons than their property of producing resinous substances. Herzog,²⁰ however, has made an elaborate investigation of these compounds with especial reference to their resinifying powers. He finds the grouping — N : C : N — to be characteristic of a whole class of substances which readily undergo polymerization with the formation of resins and may therefore be regarded as a typical resinophore group. The customary method of preparation of carbo-di-imides was that of heating a benzol solution of thiourea with a heavy metal oxide or carbonate (lead oxide, mercury oxide, lead carbonate) to remove the sulphur. The method was not reliable and Herzog²¹ improved the process by using arsenic trioxide as a desulphurizing agent. Further experiments by Herzog showed, however, that the mere heating of the thiourea without any desulphurizing agent (the temperature being carried above the melting point) serves to desulphurize these bodies and form the corresponding carbo-di-imide in a polymerized state. At the same time a small amount of the base in the thiourea is liberated. The reaction which takes place may be expressed in general terms as follows:



The polymerized carbo-di-imides are mostly brown resins and are obtained by the above reaction in good yield. They dissolve freely in most of the common organic solvents such as benzol, chloroform, carbon tetrachloride, trichlorethylene, oil of turpentine and fatty oils. On evaporation of a solution in a volatile solvent the resin remains as a glossy varnish-like coating.

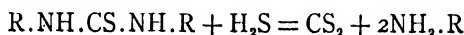
s-Diphenylthiourea ($\text{NH.C}_6\text{H}_5.\text{CS.NH.C}_6\text{H}_5$) having a melting point of 154°C . was heated in a flask in an air bath for 35 to 40 hours at $200\text{--}205^\circ$, the temperature being taken with the thermometer bulb immersed in the molten liquid. Hydrogen sulphide was given off con-

¹⁹ See also Schaal and Paschowetsky, Ber. 1892, 25, 2880; Schaal 1893, 26, 3064; 1894, 27, 2260 and 2696; Miller and Plöchl, Ber. 27, 1283.

²⁰ Oester. Chem. Z. 1921, 24, 76.

²¹ Z. ang. Chem. 1920, 140.

tinuously and also slight quantities of aniline according to the reaction



At the end of the heating period the product was distilled in a vacuum to remove any aniline still present. Carbo-diphenylimide in a condition of high polymerization was obtained as a brown brittle resin soluble in benzol, oil of turpentine and fatty oils. The yield amounted to about 65 per cent of the theoretical. During distillation in vacuum, it is probable that some depolymerization occurs. That fraction distilling at about 219° C. under a pressure of 30 mm. solidifies on cooling to a transparent amber-yellow brittle resin which appears identical with that prepared by Weith²² and considered by him to be carbo-diphenylimide. The aniline recovered from the process may be used in the preparation of thiourea by treatment with carbon bisulphide.

In carrying out the process of removal of sulphur very favorable results are obtained when a solvent having a high boiling point is employed as a diluent. Aniline is desirable for the purpose. Thus Herzog heated s-diphenylthiourea with approximately an equal quantity of aniline for 40 hours under reflux condenser. The aniline was removed by distillation *in vacuo*. From 76 grams of thiourea compound employed 43.5 grams of a fraction distilling between 190-240° C. at 30-40 mm. was obtained. This distillate solidified on cooling to an amber colored resin. The residue amounted to 8 grams and was a dark brown resin having approximately the solubility of the distillate. The melting point of the resin was 144° C.

s-Diparatolylthiourea ($CH_3.C_6H_4.NH.CS.NH.C_6H_4.CH_3$), melting point 178° C., was heated to 210-220° C. At the close of the heating period a small amount of para toluidine was removed by vacuum distillation. A brownish black resin was obtained and when subjected to distillation yielded a fraction of amber-yellow color boiling at 230° C. at 30 mm. According to Herzog this compound is similar to carbo-diparatolylimide obtained by Will.²³ If the removal of the sulphur is carried out in the presence of para toluidine as a diluent a smaller proportion of residues which cannot be distilled results.

Mixed Thiourea Resins.

Instead of the simple thiourea products, mixed resins can be obtained by using a mixture of bases. For example, crude toluidine containing aniline in addition to ortho and paratoluidine can be employed to make a composite thiourea product. On heating this material for 40 hours with subsequent removal of any uncombined base by treatment in *vacuo* a brittle brown resin is obtained which is in part capable of distillation in *vacuo* yielding an amber-colored resin. This consists of a mixture of the three carbimides. When the reaction is carried out in the presence of toluidine as a diluent the greater part of the crude resin can be distilled. The distillation temperature ranges between 190 and 240° C. when applying a vacuum of 30 mm.

²² Ber. 7, 11.

²³ Ber. 14, 1488.

Non-crystallizing Thiourea Resins.

The simple resins of the carbodiphenylimide type on standing for a long period show a tendency to depolymerize or otherwise change in such a manner as to yield crystalline products. This is probably due to a reversion to the monomolecular form of carbimide. The mixed resins, however, do not show this same tendency to crystallize and their solutions may be kept for an indefinite period without indications of change to the molecular form. Hence such composite resins are better adapted for varnish manufacture than the simpler types.

s-Phenylparatolylthiourea ($\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$). This compound was resinsified in a similar manner by protracted heating, the temperature being about 180°C . Some aniline and paratoluidine were split off and these compounds were removed from the resin by distillation in vacuo, leaving a brown resin resembling ordinary rosin. A portion of this distilled at 200°C . under a pressure of 30-40 mm. The compound, according to Herzog, is identical with carbophenylparatolylimide described by Huhn.²⁴

s-Diparachlorphenylthiourea ($\text{Cl}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{Cl}$). The melting point of this compound is 168°C . and to remove the sulphur 30 hours' heating at 200 - 210°C . was employed. Only a small amount of parachloraniline was split off. The resinous product obtained was dark and brittle. It was soluble in chloroform. The product may be regarded as a carbo-diparachlorphenylimide.

Aliphatic Thioureas.

Herzog's method is also applicable to the formation of resins from thioureas containing aliphatic as well as aromatic groups. Thus s-allylphenylthiourea $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_3\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ having a melting point of 103°C . when heated at 170 - 180°C . was desulphurized, forming a brittle resin dark in color and soluble in chloroform. Small amounts of allylamine and aniline were liberated during the reaction. The product is presumably carbophenylallylimide in a polymerized state.

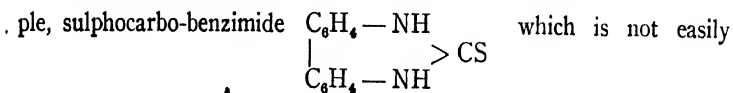
s-Di alpha naphthylthiourea ($\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$) yielded a black resin soluble in benzol on heating at 220 - 230°C . to desulphurize. A small amount of naphthylamine was liberated. The yield was nearly quantitative. The product cannot be distilled. It is probably identical with a polymerization product of carbodi alpha naphthylimide obtained by Huhn (l. c.).

s-Di beta naphthylthiourea having a melting point of 192 - 193°C . on protracted heating at 230 - 240° also yielded a resin.

s-2, 4-Dimethylphenylthiourea, $(\text{CH}_3)_2\text{C}_6\text{H}_3\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_6\text{H}_5(\text{CH}_3)_2$, melting point 152°C ., was desulphurized at 185°C . and on removal of some meta xyldine which was liberated during the reaction a resin of brittle character, of yellowish brown color and somewhat resembling ordinary rosin was obtained.

s-Dibenzylthiourea $\text{C}\cdot\text{S}(\text{NH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5)_2$, melting point 148°C ., was desulphurized by heating for 30 hours at 220°C . Some benzylamine which had been liberated was removed by distillation in vacuo. The brown brittle resin obtained exhibited the properties of carbophenylimide. The resin may be looked upon as a polymerized form of carbodibenzylimide.

Herzog calls attention to the fact that this simple method of desulphurization may be applied to the treatment of compounds which are not readily desulphurized by metallic oxides or carbonates. For example, sulphocarbo-benzimide

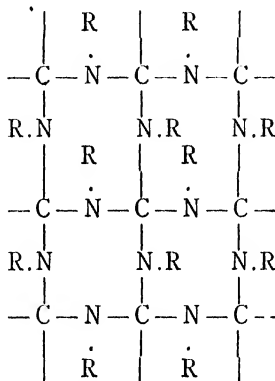


desulphurized by treatment with metallic oxides will, however, give up sulphur as hydrogen sulphide on heating to 290°C ., affording a brittle

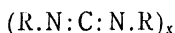
²⁴ Ber. 19, 2406.

black resin which is soluble in pyridine. The yield is 95 per cent. The imide of pinacolythiourea was obtained by protracted heating, this substance being a black lustrous resin soluble in chloroform and hot turpentine. A good varnish was made from it.²⁵

Regarding the constitution of highly polymerized carbo-di-imides Herzog calls attention to the hypothesis of Standinger²⁶ relating to the structural character of polymerized substances such as paraformaldehyde, metastyrol and rubber. Herzog proposes a structure of a similar character for the polymerized carbo-di-imides, namely,



Thus the resinifying reaction results in a body simply expressed by the following formula



Biginelli²⁷ found that urea and aceto-acetic ether combine to form β -uramido-crotonic ether. This material when boiled with dilute caustic potash forms a slightly soluble non-crystalline yellow powder, the nature of which was not ascertained.

Phosphor Resins.

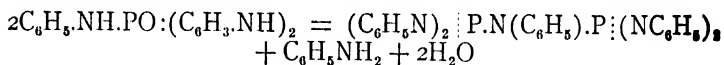
Herzog also was able to prepare a resin from a phosphorus compound, namely, triphenylphosphamide, when this compound was heated at 250-260° C., a current of carbon dioxide being passed through the compound, water and aniline were split off and a brown brittle resin was obtained. A solution of this resin in pyridine was tested by

²⁵ The interaction of aldehydes and thiourea (thiocarbamides) has been investigated by Dixon and Taylor (Trans. Chem. Soc. 1916, 109, 1244). Voswinkel (U. S. Pat. 828,908, Aug. 21, 1906) obtained a product claimed to have therapeutic value by the action of formaldehyde on urea and brominated tannin. For other compounds derived from thiourea, changing from a liquid to a solid on heating see Arndt, Milde and Eckert, Ber. 1921, 54B, 2236; Chem. Abs. 1922, 1073.

²⁶ Ber. 53, 1082.

²⁷ Ber. 1891, 1317.

Herzog for varnish purposes and the coating was found to have a considerable degree of durability. The reaction taking place during the heat treatment may be expressed as follows:



Herzog is of the opinion that the resinophore group in this case presents

the following structure:
$$\begin{array}{c} \text{N} - \\ // \\ \text{P} = \text{N} - \\ \backslash \end{array}$$

Apparently the above method represents the first deliberate attempt at preparation of a resin the essential element of which is phosphorus.

Chapter 14.

Resins from Wood and Wood Distillation.

The resins considered in this chapter do not occupy a relatively important place when considering other sources of artificial resins. Their dark color or brittle character or amount of impurities militate against widespread use. They may be employed, however, to a limited degree in the varnish and paint industry and to some extent replace better sorts of resins for other purposes.

Pagés Camus et Cie. and P. Bardy¹ recommend a process of obtaining artificial resins by the interaction of the "phenolic oils," "aldehydic oils," and "aldehydic residues" formed in the distillation of wood or analogous products, preferably in the presence of an acid or alkaline condensing agent. Thus the pyroligneous vapors from the distillation are mixed together at a temperature below 250° C. (acid condensation). The vaporized products are then treated with a substance having alkaline reaction, and the resulting resins are dissolved (alkaline condensation). Finally, the solution is neutralized with an acid. The three stages may be carried out successively so as to obtain the different kinds of resins formed in each condensation, and special types of apparatus are used for the different modifications of the process. An alternative process is to render alkaline the mother liquors from the crystallization of pyroligneous solutions, and to submit them to the general methods of condensation mentioned above, thus obtaining resins, acetates, and higher fatty acids (butyric acid, etc.). Another modification is to treat the pyroligneous vapors with an insoluble salt (e.g., calcium carbonate), which is not acted on by phenols but is decomposed by acids. The crude acetates resulting from this process may then be separated and purified. They² also describe a process for manufacturing resin-like condensation products by leading the hot distillation products of wood, freed from tar, through an alkaline solution, e.g., milk of lime, and acidifying the resulting solution after filtration. The acidification can be effected by the introduction of acetic acid containing distillation gas until the desired results are obtained.

Duchemin,³ in discussing aldehyde resins obtained by carbonization of wood in closed vessels, refers to the discovery of these resins by D. and P. Bardy, while studying a method of preparing acetates by the

¹ J. S. C. I. 1909, 1320; French Pat. 402,907, Sept. 9, 1908.

² Chem. Abs. 1911, 3175; German Pat. 234,806, Sept. 23, 1908.

³ Bull. Soc. Chim. 7, 473; J. Chem. Soc. 98, 462; Chem. Abs. 1910, 2873; Chem. Centralblatt 1910, 11, 604.

direct absorption by means of alkaline carbonates.⁴ The solutions obtained deposited a black, amorphous, plastic residue when acidified. When this was heated to about 200° C. a solid, black mass of conchoidal fracture resulted. The same product is obtained when crude pyroligneous acid, decanted from the tar, is boiled several hours under a reflux condenser, and also when the heavy phenolic oils obtained by distilling pyroligneous acid are heated with formaldehyde in the presence of hydrochloric acid. An oily liquid is obtained in the redistillation of crude methyl alcohol which, on adding sodium hydroxide, is converted into a light yellow resin. To get the largest yield of resins, each absorption vessel must be connected with a battery of retorts instead of a single one, so that phenolic vapors coming over near the end of the distillation in one retort will meet the aldehydic vapors arising at the beginning of the distillation in the next retort. The resins, on heating to temperatures above 200° C., finally swell up and form a light coke. They are soluble in alkaline solutions, and are re-precipitated by acids, and are also soluble in a number of organic solvents, the solubility of the resins which have been heated to higher temperatures being less. In distilling crude methyl alcohol over an alkali, light-yellow resinous substances are obtained, which turn brown on exposure to air, and are insoluble in alkaline solutions. These resins cause methyl alcohol to turn brown on long standing. Other resins are also obtained in the preparation of alcoholates, e.g., from the mother liquors of sodium alcoholate. The total amount of resins obtained is reported to be about 5 per cent of the wood charred. These resins not only have some commercial value, but their separation also renders the other products more easily purified. The suggestion has been offered that the tars formed in the dry distillation of wood are merely solutions of resins in phenols which have not been acted upon. Duchemin also succeeded in isolating pure acetaldehyde from the aldehydic substances obtained in the dry distillation of wood.

Between the retorts and the condensers used in carbonizing wood in closed vessels, Duchemin⁵ interposed a series of saturating vessels in which the pyroligneous vapors, previously freed from tar, were treated with an alkali carbonate. The liquors which were collected in these vessels were dark at first, but turned yellow on becoming acid, and then deposited a black, plastic amorphous magma which contained small quantities of water and of acetates. On heating, this resinous product melted at about 60° C., lost its water, and if heating was stopped at about 200° C. it cooled to a black, hard mass exhibiting a conchoidal fracture. If the saturators are connected to only one retort, a very small proportion of resin is obtained, owing to the fact that the bulk of the aldehyde products is liberated before the phenolic products. The saturators are best connected to three or four retorts in which distillations are started at intervals of 12 or 24 hours, as by this arrangement

⁴ French Pats. 375,314 and 402,997.

⁵ Bull. Assoc. Chim. Sucr. et Dist., 1910, 27, 1101; J. S. C. I. 1909, 1320; and 1910, 748.

the interaction of the aldehydic and phenolic products is very complete. The removal of the resins in the saturating vessels facilitates the preparation of white sodium acetate and the purification of the methyl alcohol.

Chute's Resin.

One method used in treating pyroligneous liquor is first to distil the whole bulk of volatile liquid to get rid of non-volatile impurities and tarry substances. This distillate is barely neutralized with lime to form the acetate, and alcohol which is present is distilled from the neutral liquid. It is necessary to guard against the use of an excess of alkali because of its polymerizing and resinifying effect. The presence of such polymers or resins would contaminate the acetate of lime. Chute⁶ fractionates pyroligneous acid to obtain a distillate containing from 10 to 25 per cent of alcohol. In this distillate Chute finds substances which are quite sensitive to the action of alkali and which he regards as, probably, largely ketonoid or aldehydic in their nature and which with alkali polymerize or resinify to form tarry insoluble bodies. On the addition of an alkaline substance, such as lime, reaction sets in as indicated by the development in the distillate of a yellow color. As the reaction progresses resinous matters precipitate. These resinous bodies form a product which Chute terms a "dye-resin" being susceptible of use as a dyestuff as the product stains organic matters a bright yellow when properly applied and also is of use as a resin. In view of the subsequent trend of development of synthetic resins from aldehydic substances, the observations of Chute in 1906 are of significance.

Other Resins.

Klemm⁷ examined a sample of liquid oil-resin, obtained as a by-product from sulphate wood pulp mills and found it capable of serving as a partial substitute for colophony.

An asphaltic substance⁸ separated from wood tar by sulphuric acid⁹ is soluble in alcohol, wood spirit, acetone, etc., and may be used either alone or in conjunction with other resins soluble in spirit for the preparation of lacquers, etc., which have antiseptic, waterproofing and insulating properties.

According to König¹⁰ when wood is treated under pressure in a digester with dilute mineral acids or with dilute alkalies, a liquid which is separated is rich in sugar. Resin can be recovered from the sugary liquid by neutralizing it with ammonia, etc., or by neutralizing with

⁶ U. S. Pat. 824,906, July 3, 1906.

⁷ Chem. Z., 1910, 34, 1353; J. S. C. I. 1911, 37.

⁸ Chem. Fabr. Florsheim H. Nordlinger, J. S. C. I. 1916, 610; German Pat. 290,818, July 17, 1914.

⁹ German Pat. 286,650; J. S. C. I. 1916, 106.

¹⁰ Chem. Abs. 1916, 75; British Pat. 8,006, March 30, 1914.

calcium carbonate the extract obtained when dilute sulphuric acid is used, and allowing the resin to separate.

Aktiebolaget Cellulose¹¹ heat wood rich in resin, such as Swedish pine, under pressure with sufficient concentrated alkali solution and with the addition of a soluble neutral salt such as sodium chloride. The wood dissolves and the resin is converted into the alkali salt of the resin acids. Fatty acids and lignin, precipitated together with the resin, are soluble in alcohol and sufficiently resemble the resin in their properties to have no observed deleterious effect upon the product. Oil of turpentine, methyl alcohol, ammonia, and amines distill over if the vapor is allowed to escape during the heating.

According to Hamburger¹² resins may be prepared by heating wood tar with the oxides of heavy metals, e.g., with zinc oxide at about 110° C., and then for a short time at a higher temperature. From 10-12 per cent of zinc oxide can be absorbed by the tar without injuring the properties of the resin.

Riedel¹³ found that if wood tar is heated and agitated in the presence of a halogen, with or without the addition of a catalyst (aluminum chloride), a brittle dark resinous mass results when cooled. The product dissolves in alcohol, giving a rapidly drying varnish.

Noerdlinger¹⁴ also produces a quick-drying varnish as follows: Pine tar is freed, by distillation, from the constituents boiling below 200° C., the distillation residue is hardened by lime and the product dissolved to produce varnish. The distillation may be effected under reduced pressure, or in a current of air or steam. For example, 1000 kilograms of light pine tar are distilled at 100-160° C. with superheated steam, until oily constituents are no longer contained in the distillate. About 700 kilograms of a viscous residue and about 200 kilograms of a light distillate containing turpentine oil are obtained. The residue is hardened with 5 per cent calcium hydrate at 160-200° C. and then dissolved in a solvent. The resulting varnishes vary from light to dark brown in color, dry rapidly and with a gloss, without being tacky, and exhibit antiseptic and preservative action on wood.

According to Hartmuth,¹⁵ in producing artificial resins from wood or cellulose materials, inorganic or organic acids, or acid substances with the exception of hydrochloric acid, may be employed as catalysts. The following catalysts for the phenolic digestion process are suggested by him; ammonium salts, stannous, stannic, aluminum, and zinc chlorides, silicon tetrachloride, and nitro and chloro-phenols.

The alkaline liquor obtained by heating comminuted wood with sodium carbonate deposits on cooling a sludge containing resin soap and lignin. According to Lange¹⁶ this is separated from the supernatant

¹¹ German Pat. 315,731, May 20, 1916, J. S. C. I. 1920, 307A.

¹² J. S. C. I. 1920, 792A; German Pat. 324,876, Dec. 12, 1917.

¹³ J. S. C. I. 1920, 633A; German Pat. 320,620, July 11, 1918.

¹⁴ J. S. C. I. 1920, 633A; German Pat. 320,656, April 16, 1916; Chem. Abs. 1921, 1083.

¹⁵ J. S. C. I. 1921, 212A; German Pat. 328,783, Nov. 27, 1919.

¹⁶ German Pat. 314,445, April 30, 1918.

liquor and warmed with sodium hydroxide, whereupon the soap forms large flocks, which are collected and treated with a small quantity of sodium peroxide to oxidize any lignin still present. The liquid containing dissolved lignin is evaporated to recover the excess of soda by crystallization, and may then be used as a binding agent in the manufacture of briquettes.

Aschan and Ekholm¹⁷ isolated pinabietic acid, $C_{20}H_{30}O_2$, from sulphite-cellulose liquors after the removal of fatty acids, in the form of glittering needles, melting point $176-178^\circ C.$, which readily resinify.¹⁸

In the treatment of esparto grass to obtain cellulose a black liquor results which contains a large amount of organic "extract matter." Budde¹⁹ found that a slight excess of acid or treatment with chlorine gives a slimy, finely divided precipitate almost impossible to separate from the mother liquor, but treatment of the boiling black liquor with a large excess of acid, e.g., sulphuric acid, gives a coagulated, resinous precipitate easy to separate. The resin is soluble in acetic acid, acetone, phenol, alcohol, aniline and alkalies, but insoluble in ether, oils or turpentine. The suggestion has been made that this resin may be used for sizing and waterproofing purposes and as a varnish.

¹⁷ Finska Kemistsamfundets Meddel., 1918, Chem. Zentr., 1919, 90, I, 285; J. S. C. I. 1919, 646A.

¹⁸ Note also Enger, Chem. Abs. 1918, 12, 94; Norw. Pat. 28,084, July 16, 1917.

¹⁹ J. S. C. I. 1916, 35, 401.

Chapter 15.

Hardened Rosin and Resinates.

Within the last decade or so the art of varnish-making has been completely revolutionized by the extensive introduction of tung or Chinese wood oil varnishes. Previous to this time much rosin had been used for the adulteration of varnish gums, and, in the form of "gloss oil," as a cheap and deleterious addition to paints and enamels. Gloss oil is a solution of lime-hardened rosin in mineral spirits.

It has been realized for some years that rosin has wonderful adaptability in combination with tung polymers for the production of varnishes of great and varied utility, having remarkable properties and fair durability. The outstanding characteristics of tung-rosin varnishes are extremely pale color, great rapidity of drying, high gloss, waterproof properties and very fair durability. Accordingly rosin has risen from the position of a despised adulterant to a necessary raw material of extensive applicability. Tremendous quantities of these varnishes are used today. Some are simply tung oil, rosin and thinners; others contain proportions of linseed oil or other oils or resins.

Rosin in the Natural State.

Untreated rosin is not satisfactory for this purpose for many reasons. It is too soft, too acid and neither waterproof nor durable. Raw rosin feels sticky or tacky, even in the heat of the hand. Its softening point is about 70° C. The acid number averages about 160. When exposed to moisture it turns milky white, probably due to penetration of moisture with the formation of an emulsion film on the surface. Rosin is a plastic, non-crystalline solid. It belongs to the class of colloid bodies and its solutions are emulsoids.²

A considerable portion of the rosin used in the manufacture of varnishes is prepared by neutralizing part of the free rosin acid with slaked lime at a maximum temperature of 271° C. This treated rosin is known in the industry as "lime hardened rosin," "limed rosin," or simply as "hardened rosin." Strictly speaking, rosin so treated is not a synthetic product. Neither is it a natural resin. It is an artificial

¹The author wishes to acknowledge his very grateful appreciation of the coöperation of Mr. Alexander Murray, 750 East Ridgeway Avenue, Cincinnati, Ohio, in connection with the revision of this chapter.

²Schlick, *Farben Z.*, 1922, 27, 1439, 1511, 1583, 1650; *Chem. Abs.* 1922, 2032.

resin obtained by the chemical treatment of a natural resin and space therefore has been allotted herein to a description of the manufacture and properties of this resinous product.⁸

Tacky Qualities.

If rosin is dissolved in benzine (mineral spirits) and this solution then brushed out on some surface and permitted to dry, it will be found that when the thumb is pressed down firmly upon it the film will appear tacky. This is known as the printing effect, and persists when raw untreated rosin is used as a major ingredient in the preparation of a varnish. The latter might appear to dry satisfactorily, especially in cold weather, but in a warm room or on a hot summer day the coating is liable to become decidedly sticky. The untreated rosin varnish may have a remarkably high gloss when applied, but it becomes dulled rather rapidly. This varnish also gives inferior service outdoors. Gardner has shown that it is entirely unsuitable for concrete and cement paints, because of its very high acid number.

Effect of Heat.

It has been suggested that a combination occurs between the wood oil and rosin, with the resultant production of a new compound of indefinite composition. There is no real evidence, however, that any such reaction takes place, and, on the contrary, observation indicates that no combination occurs between the rosin and tung polymers other than physical interdispersion, and that the properties of the rosin are not changed in any absolute sense, but only modified or diluted by the presence of the tung oil. The heating to which the colophony is subjected in the cooking of the varnish is insufficient to change its characteristics to any marked extent, and such change, contrary to some opinions, tends actually to soften besides darkening it. In some recent experiments Murray found, after heating rosin for one hour at 300° C., that the acid number was reduced to 149. Since it is well known that on distillation rosin breaks down into lighter distillates, rosin oil, and tar, a lowering of melting point should be expected when it is heated to incipient distillation for any length of time. Practically all natural resins become more fusible by heating.

⁸In 1884, Kissel advocated the use of lime for raising the melting point of rosin and other resins. He also stated that other bases such as baryta or magnesia could be used instead of lime. German Pat. 30,000, 1884; U. S. Pat. 303,436, Reissue 10,714, Apr. 20, 1886; also U. S. Pat. 414,366, Nov. 25, 1890. Melvin used zinc oxide. U. S. Pat. 370,640, Sept. 27, 1887; Brit. Pat. 5270, 1886. Truchot, *Rev. Chim. Ind.* 1897, 107; J. S. C. I. 1897, 449, described the preparation of resinates. Note also J. S. C. I. 1899, 1134; Prager, *Seifen Ztg.* 1915, 705; Geutzel, U. S. Pat. 657,696, Sept. 11, 1900; Cadoret and Deligeon, J. S. C. I. 1911, 636; French Pat. 423,545, Feb. 17, 1910; Ellis and Weber, U. S. Pat. 1,381,863, June 14, 1921, have used calcium cyanamide. Bauner proposed heating a mixture of lime and sulphur in a partial vacuum. The proportions recommended are rosin 160 parts, lime and sulphur, 10 parts each, *Chim. et Ind.*, 1921, 5, 497; Brit. Pat. 188,227, 1888.

Liming.

The object of liming rosin when it is to be used in varnish is to raise its melting-point, harden it, decrease its degree of dispersion in solvents, render it more water-resistant and durable, and give a more permanent lustre to the varnish.

A varnish containing hardened rosin will set more quickly than that made with raw rosin; not because the calcium resinate is a "drier," but because raw rosin is a strong dispersing agent, or *peptizer*, of varnish colloids (tung polymers, fossil resins, linoxin, etc.). Thus, a varnish containing much free resin sets, or gels, more slowly than rosin-free varnish.

The liming of the rosin decreases its degree of dispersion, and proportionately, the undesirable inhibiting action here indicated, or, to borrow the language of Schlick, the "concentration of the colloid phase is increased," which, as he has suggested, is a preliminary condition in the physics of the drying process.

Bloom.

A bad effect of free resin acid in varnish is seen in the bluish opalescence, or "bloom," sometimes disfiguring the varnish on furniture in damp weather. This is apparently due to absorption of moisture by the resin acid in the surface.

Livering and its Cause.

"Livering" is a peculiar thickening which occurs when basic pigments, and, more especially, zinc oxide, are ground with certain varnishes. In its most characteristic stage this thickening assumes a liver-like consistency. It is due to various stages of gelation of the vehicle, and may occur immediately after grinding with the pigments or after storage for a longer or shorter time. The first is due to a purely physical reaction, occurring when a varnish containing a highly polymerized oil or gum, which is peptized (held in "solution") by resin acids, is mixed with basic pigments. This is due to the fact that a very large proportion of the free acid is absorbed by the pigment surface, and, since nothing is then left to prevent the colloids from gelling, the inevitable happens.*

The phenomenon is usually only troublesome when zinc or titanium oxides are present. With the other basic pigments gelation is usually deferred for weeks until the resin acid has reacted chemically with the oxides or carbonates. Gelation then occurs. There are other causes of thickening on storage which do not concern us here.

It will be seen, then, that free resin acid is something to be avoided in paint and varnish products. Rosin which has been treated with lime is, however, not entirely reliable as cases are on record of livering occurring in paint or enamel made from hardened rosin after standing for several months.

* Muehle, Rosicki, Megerle, *Farben Z.*, 1913, 1944, 2058, 2178, 2230.

Furniture Varnish.

On the other hand, in making a cheap furniture varnish, lime is used in the rosin to harden it so as to overcome what is called "printing" effect. The varnish has to be hard enough so that when the furniture is shipped in its paper wrappings the paper will not adhere to the varnished surface. A varnish made from acid resin is very shiny when fresh, but rapidly loses its lustre. Such varnishes cannot be "dull-rubbed." If the rosin is well hardened the lustre is more permanent, and if 9 per cent to 11 per cent of hydrated lime has been used, the varnish can be rubbed to fair advantage.

Incomplete Neutralization.

In practice, rosin is never neutralized completely by fusion with lime because complete neutralization cannot be effected in this manner. It is probable also that what lime enters into combination does not form a pure neutral resinates, but a mixture of neutral and basic resinates. To this may be ascribed the fact that the acidity is never decreased in proportion to the amount of lime used. The ratio of basic to neutral resinates appears to increase as the amount of lime is increased, and, at the same time, increasing quantities of hydrated lime become dispersed as a suspensoid in the fused mass. This suspensoid character greatly decreases the fusibility of the batch, so that it must be heated far above the melting-point of pure calcium resinate to liquefy it. At these temperatures the resinates begins to decompose (say 600° F. or 316° C.). For these reasons it is impossible to manufacture neutral calcium resinate by the fusion method. However, the neutral salt can readily be prepared by precipitation from aqueous solution. The complete neutralization of the rosin acid would make the product at least partly insoluble in the liquids usually employed in thinning, especially mineral spirits, and would also decrease the lustre of the finished product.

Fusion Method.

Lime is customarily united with rosin by fusing it with the latter. A good grade of lime should be chosen for the purpose. Oyster shell lime formerly was favored by a number of varnish manufacturers because of a supposedly higher degree of solubility in the hot resin. Oyster-shell lime is weaker in calcium oxide content than a good grade of hydrated chemical lime, but it is technically free from iron and magnesia, and of course its composition is reasonably constant. Many commercial limes contain appreciable amounts of iron, which is taken up by the rosin and discolors the product. As for magnesia, its effect is peculiar, due to the fact that solutions of magnesium resinates have much higher viscosities than solutions of the calcium salt. Very small proportions have a noticeable thickening action, which is highly undesirable, since the tung polymers themselves have great viscosity. The magnesium salt is much less fusible than the resinate of lime, which

presents an additional disadvantage if the magnesium content is high. A suitable lime should not contain over 1 per cent of magnesium oxide and should be technically free from iron. In recent years hydrated lime has come into extensive use. As found on the market, hydrated lime is a fine powder which has been well screened to remove particles of silica and other impurities and gives good results as a hardening agent. Hydrated lime is better than quick lime for hardening rosin owing to the more flocculent or voluminous condition of the hydrated lime which permits it to react quickly with the rosin. It also liberates water in combining with the rosin, and the evolution of steam serves to keep the lime thoroughly suspended in the molten rosin. Quick lime settles to the bottom and stays there. Coral lime is recommended by Scheel.⁵

Proportion of Lime.

Ordinarily not over 5 or 6 per cent of hydrated lime, based on the rosin, is used. Above this amount there is a tendency to the formation of resinates which are insoluble in paint and varnish thinners. When hardened rosin, which has been over-limed, is thinned with oil and turpentine or naphtha the hardened product may dissolve completely but subsequently separates in part on storage, forming sludge, which is, of course, highly objectionable. If the rosin is not cooked sufficiently with the lime, or when too much of the latter is used, considerable quantities of calcium hydroxide are suspended in a colloidal condition, giving the varnish a milky appearance which persists stubbornly through the clarifying operations.^{5a}

As stated, the quantity of lime used is ordinarily between five and six pounds of dry hydrate per hundred pounds of rosin. Zimmer⁶ has recommended the use of nine to eleven parts of lime to one hundred parts of rosin. Murray also recommends the use of 11 per cent of lime in quick drying varnishes. The permanency of varnishes containing so great a proportion of lime apparently depends on the extent to which the oils have been cooked and the dispersing power of the thinner. The dispersing power of various petroleum naphthas of the same boiling point range is reported to vary within wide limits. Using straight petroleum thinners there will frequently be some cloudiness which is not removed by repeated centrifuging and therefore represents a coarse sol. Such a condition in time may lead to sedimentation. Hydrated lime averages about 65 per cent calcium oxide. Better grades contain 70 per cent and over of the oxide. Assuming that all of the lime present as hydroxide (5-6 per cent) was taken up by the rosin there should be present approximately from 3.2 to 3.9 per cent

⁵ U. S. Pat. 1,428,120, Sept. 5, 1922.

^{5a} The addition of one per cent of soda ash during the melt is considered by some a desirable procedure to assist in holding the lime resinate in solution. Rosin so treated is very easily affected by water and the custom is not to be recommended.

⁶ *Chim. et Ind.*, 1921, 5, 497.

CaO in the finished product. The lime present as carbonate is not acted upon readily by molten rosin.

The amount of lime taken up by rosin is illustrated by the following:

	<i>Lbs. Hydrated Lime per Cwt. of Rosin</i>	<i>% CaO Found on Inciner- ating</i>	<i>Direct * Atid No.</i>
Hard W. G. Rosin.....	5 lbs.	3.0%	105.6
Extra Hard W. G. Rosin.....	9 lbs.	5.3%	83.8

* Milligrams KOH per gram.

The following is a typical working formula:

Melt 500 lbs. of W.G. rosin and at 420° F. (216° C.) add 30 lbs. hydrated lime. Raise to 520° F. (271° C.) and hold 15 minutes or longer until the lime has been taken up, drop to 450° F. (232° C.) and dip out into clean iron pans.

In connection with the working temperatures given above, which are those in extensive use in the industry, it should be mentioned that hot rosin darkens rapidly in contact with the air, and since pale color is ever desirable and nothing is gained by high temperatures, it should be subjected only to the lowest practicable temperatures for the shortest possible time. This rule should be observed at all times when cooking rosin. It darkens more quickly than heated oils, and therefore it should be added to the batch of varnish at as late a point in the cooking as possible. When using 6 lbs. of lime to 100 lbs. of rosin, the latter may be heated to 400° F. (204° C.), the lime then added (it need not be sifted) and thoroughly stirred in for about ten minutes, when the operation will have been completed.⁷

Higher Proportions of Lime.

It is not possible to prepare pale hardened rosin with much less than 30 per cent of free rosin, because of the high melting point of the rosinate, and in order to get even this degree of neutralization it is necessary to cook the rosin with 9 lbs. of lime per 100 lbs. of rosin at a temperature of 435 to 440° F. (224-227° C.) for one and one-half hours. In this case one would, of course, keep the kettle covered during the cook.

Other Details.

Rosin can be subjected to a great deal of cooking in covered aluminum kettles without darkening at all, and the rosin acids do not appear to attack the metal to any marked extent. If the hardening is being conducted as an integral part of a varnish cook, the next ingredient is added as soon as the lime is combined; and if being limed separately, the hardened rosin is ladled into shallow pans to cool, and then broken up and stored for future use. The advantage of liming

⁷ Murray, Chem. Met. Eng. 1921, 25, 473.

large batches of rosin at a time is, of course, primarily the saving of labor and fuel, but it also facilitates uniformity, since it is possible for the laboratory to follow the neutralization closely, and make corrections when necessary. In case the oils have to be cooked for an hour or longer it is advisable, from the point of view of the color of the product, to have the rosin already hardened and add it at a late stage of the cooking.

Cloudiness and Deposits.

Rosin hardened with 6 or 7 per cent of lime should be transparent but as the percentage is increased the product becomes more cloudy. It is easily soluble in fatty oil rubbing varnishes with Congo and other hard gums, and alone with Chinese wood oil in other types of varnishes. Since hardened rosin has not the same retardant action on the polymerization of tung oil exhibited by untreated rosin, such varnishes must be made at lower temperatures. Hardened rosin varnishes are still unsuitable for use in concrete, plaster and cement coatings, since they contain considerable free rosin acids. They also caused serious thickening when used with zinc oxide and some white leads and lithopones before this reaction was better understood. Furthermore, hardened rosin is very brittle and imparts its brittleness to a varnish to an extent proportional to the amount used.

Rosin Oil.

The introduction of rosin oil recommended by Pirschl⁸ in hardening rosin is to be deprecated, as it is a decidedly deleterious constituent of protective coatings, and, in fact, its practical use is very rare in this connection. Large quantities of rosin oil are prepared for the manufacture of lubricating greases. "D" grade rosin will yield by distillation about 65 per cent by weight of rosin oil of acidity 46-47 per cent, calculated as rosin acids. There results at the same time 7-8 per cent rosin spirits of 3.5 per cent acidity.

Water Resistance.

Hardened rosin is extensively used with Chinese wood oil to make a low priced varnish which will withstand water. A dried coating of gloss oil very promptly turns white on contact with water. The same is true to a lesser degree with linseed oil-rosin varnish. The Chinese wood oil or tung oil-rosin varnish is highly resistant to water. Moreover rosin acts as a good solvent for over-heated or gelatinized tung

⁸ An additional quantity of lime may be combined with rosin, according to Pirschl (U. S. Pat. 521,270, June 12, 1894) by adding rosin oil as a flux. The addition of 10 lbs. of the oil to 100 lbs. of rosin enables complete combination of 8 lbs. of lime. Pirschl claims to have made various products, one of which contained 16 per cent of manganese dioxide, another contained 10 per cent of barium oxide. One compound contained 40 per cent of lead oxide. Oxides of iron, copper and zinc from 2 per cent and upwards likewise could be prepared.

oil, a fact often of importance to the varnish maker. Rosin also serves to prevent the frosting or whitening of tung oil varnishes containing harder resins such as manila or congo gum. Hence wood oil and rosin are notably useful in admixture and as stated, varnish preparations of this character are very widely employed.

Gloss Oil.

This is about the cheapest variety of varnish known and consists simply of hardened rosin reduced with mineral spirits. Using the formula just mentioned, the lime and rosin are held at 510° F. (266° C.) until combined, the temperature is dropped to 240° F. (116° C.) and the mass reduced with 60 gallons of mineral spirits. This yields about 100 gallons of finished product. Gloss oil is used to a considerable extent as a grinding liquid, with bodied linseed or other drying oils, in the manufacture of flat white enamels. Made with darker grades of rosin it is used as a primer in painting plastered walls. Further uses of gloss oil are in cheap lacquers, tool varnishes, shingle stains, bronzing liquids, liquid driers, etc. Gloss oil paint films turn yellow with age, and its inclusion in flat white paints, enamels, undercoats, etc., is attended with serious risks of "yellowing." Ordinary gloss oil (6 per cent lime) contains 40-45 per cent free rosin acids, and is not to be recommended as a sizing material, since it will cause ultimate dusting or crumbling of plaster or cement surfaces.

Rosin Neutralized by Other Basic Oxides.

Magnesia.

This base has been recommended as a hardening agent but is more costly and has no technical advantage over lime. On the contrary it tends to produce a resinate which is more insoluble in mineral spirits and consequently more difficult to filter. This is also true of limes containing a high percentage of magnesia.

Magnesia and Zinc Oxide.

Although magnesia is considered an undesirable constituent of hydrated lime when used for hardening rosin in the usual manner, a mixture of magnesium oxide and zinc oxide has been used for hardening rosin for grinding varnishes and has given generally satisfactory results. About 2 per cent of magnesium oxide and 5 per cent of zinc oxide are used based upon the weight of rosin taken. The reaction between the rosin and the bases is carried out at about 450-500° F. (232-260° C.). A good mixing varnish can be made from this type of hardened rosin.

Zinc Oxide.

This oxide is used to some extent but some varnish makers believe it will combine effectively with rosin only by previously adding lime. Zinc oxide, having a higher molecular weight, has to be used in greater proportion than lime; but this is practically offset by the fact that the compound contains nearly 100 per cent oxide against 65 per cent CaO in commercial hydrated lime.

The usual ratio is four pounds slaked lime and from two to three pounds high-grade zinc oxide per hundred pounds of rosin. Zinc-lime resinate is used principally in rubbing varnishes.

Reduced Zinc-Lime Rosinate.

In the manufacture of cheaper grades of enamels where a light color is desirable, "gloss oil" can be made with an excess of zinc, using a steam jacketed kettle provided with a stirring device, instead of a fire heated varnish kettle.

The following is a typical formula:

Melt 1500 lbs. W. G. Rosin in a steam jacketed kettle,
Add 45 lbs. Slaked Lime, commence stirring, then add
75 lbs. Zinc Oxide.

Agitate at a maximum temperature of 300° F. (150° C.) until the mixture gives a clear drop on glass (4 to 5 hours), then cautiously reduce with mineral spirits, with constant stirring until 185 gallons have been added. The yield is about 325 gallons. This product has a pale color and a low acid number.

Action of Lime on Other Resin Acids.

Various proposals have been made for hardening resins other than rosin by lime treatment. In one case a hardened product was made from fused Congo gum, having an acid number of about 65. The amount of slaked lime was calculated so that the resin acids would be nearly neutralized. The lime combined easily and the product did not become pasty as easily as rosin, due to the high amount (about 30 per cent) of unsaponifiable matter present, which acted as a flux. However, after being exposed to the air for several months, the carbon dioxide of the atmosphere had combined with the lime breaking its weak combination with the Congo resin acids, thus forming an effloresced mass of free resin acids and calcium carbonate. Such a reaction never takes place with lime or zinc hardened rosin. The only other calcium resinate of much commercial importance is limed dammar, which is extensively used, frequently in conjunction with hardened rosin.⁹

Testing Lime.

To determine whether lime is suitable for use in varnish making Gardner¹⁰ recommends the gloss oil test method. This test is carried out by melting 50 g. of rosin at 360° F. (182° C.), adding 2 g. lime, raising the temperature to 500° F. (260° C.), cooling to 400° F. (205° C.) and thinning with 50 g. mineral spirits. In this test, observations are made on the rapidity of the reaction, clarity of the mass, amount of sediment, and body. A determination of the acid number of the varnish also is made. A method employing tung oil consists of stirring 1 g. lime into 50 cc. raw tung oil, and heating. Good lime usually starts to react at about 175° F. (80° C.). Continue heating to 284° F. (140° C.), cool and observe the amount of insoluble tung oil soaps formed. Gardner notes that carbonate of lime is practically insoluble in varnish stock. High magnesia limes give heavy-bodied varnishes that are inclined to be turbid or to precipitate, although magnesia neutralizes rosin as well as lime. Soft, finely divided lime reacts more readily than hard, coarse, over-burned lime. A suggested tentative specification for hydrated lime for use in varnish is: color, white; fineness, not more than 10 per cent retained on a 250-mesh screen; reactivity, satisfactory in gloss oil and tung oil heat tests; CaO, not less than 70 per cent, fully hydrated, equivalent to 92.5 per cent Ca(OH)₂; MgO not more than 3 per cent; Fe₂O₃, Al₂O₃, and insoluble matter, not more than 2 per cent; CO₂, not more than 2 per cent.

Fused Resinate Driers.

The oxides of lead, manganese, and cobalt, when fused with rosin, are used to a considerable extent as driers in varnishes, especially in

⁹ Dammar may be hardened by treatment with 2-5 per cent of lime and the acidity of manila or kauri gum can be diminished by similar lime treatment. *Chim. et Ind.*, 1921, 5, 497.

¹⁰ Paint Manufacturers Association of U. S., *Circ.* 113, Jan., 1921; *Chem. Abs.* 1921, 765; see also Circular 120 on Metallic Soaps.

cases where the drier has to be added after the oil has been boiled. In such cases the oxides themselves could not be used.

These metallic resinates are made to contain between two and three per cent metal for manganese and cobalt, and from nine to ten per cent for lead. The hydroxides of manganese and cobalt are more easily taken up by the rosin than manganese peroxide or tri-cobalt tetroxide. As in the case of zinc oxide, the previous incorporation of lime apparently keeps these catalytic driers in solution better than when the lime is not used.

Precipitated Resinates.

The preparation of resinate driers by fusion is an inefficient practice which should be obsolete. The neutral resinates, of definite composition, can be prepared quantitatively by precipitation from solutions of the salts, and, so prepared, have least effect on the color of the varnish. Organic solutions of organic driers are all suspensions, and gradually deposit flocculent material on storage in the dark. The flocculation is accelerated in daylight. The drying power of these liquid driers decreases markedly as the degree of dispersion decreases.

A common practice is to use lead and manganese together in the ratio of three parts lead to one of manganese, or as high as five parts lead to one of manganese. There is at least one very successful drier containing approximately Lead 20, Manganese 1, Cobalt 1.

The following is a practical working formula for a lime, litharge and manganese melt:

Melt 500 lbs. F. Rosin at 400° F. (204° C.).

Add 20 lbs. Hydrated Lime.

Raise to 520° F. (271° C.).

Drop to 400° F. (204° C.).

Then add 50 lbs. powdered Litharge, 15 lbs. fine Manganese Dioxide.

Raise to 450° F. (232° C.) and hold between 450-460° F. (232-238° C.) until taken up, then dip out into clean iron pans.

The fused resinates of iron, chromium, aluminum, and other oxides have been used in the varnish industry but they are of no importance, either as hardening agents or driers. Fused nickel resinate has lately been tried as a drier but its value has not been definitely established.

Flattening varnishes have been made by grinding aluminum or lime soap into a quick drying varnish such as Chinese wood oil and rosin varnish. Aluminum palmitate is preferred. The varnish must be of the quick drying type because the palmitate retards the drying. On standing for an indefinite period some reaction takes place so that the flattening effect is lost. All flattening varnishes made on this principle are inferior.

Ruth and Asser¹¹ advocate the use of naphthenic acid for the production of driers and linseed oil substitutes. Naphthenates soluble in solvent naphtha and applicable as siccatives are obtained by heating naphthenic acids with oxides or carbonates of chromium or aluminum at 464°-500° F. (240°-260° C.) and expelling any unsaponifiable matter at 662° F. (350° C.), or by precipitation of an

¹¹ German Pat. 327,374, Feb. 18, 1919, and 327,375, June 21, 1919; J. S. C. I. 1921, 187A.

alkali naphthenate with an aluminum or chromium salt, washing and drying the precipitate and finally fusing it at 464°-662° F. (240°-350° C.). By heating aluminum or chromium naphthenate with magnesia, calcium hydroxide, or zinc oxide at 392° F. (200° C.) or at 320° F. (160° C.) under a pressure of 10 atmospheres, products are obtained which alone or mixed with other naphthenates, resins, drying oils, or marine animal oils can be used as siccatives, or as a substitute for linseed oil varnish or oxidized linseed oil.

Metallic Soaps.

Those compounds of the metals with fatty acids and resins which are insoluble in water are known as metallic soaps and find extensive use in varnish manufacture, driers, waterproofing compositions and various other products, along with or in substitution for the natural resins. Although insoluble in water they dissolve in varying degrees in organic solvents such as benzol, solvent naphtha, turpentine, petroleum spirits and oils.

The scope of the present volume does not permit of a discussion of driers as the uses of these are not strictly speaking in the domain of synthetic resins.

Aluminum and magnesium soaps are used in the production of colorless waterproofing compositions. Aluminum oleate, owing to its power of forming thick jelly-like solutions, has been recommended very frequently as a thickening agent but in the author's experience is not very satisfactory owing to a reduction in viscosity occurring on keeping which in some solvents is marked.

Aluminum and magnesium soaps are also used in flat varnishes and as additions to mixed paints to produce a fictitious body and suspensory effect. Barium soap has been used for its weighting effect. The author has used lead stearate advantageously to increase the melting point of waxes for certain purposes.

Copper soaps have been used in antifouling paints and wood preservatives. Iron soaps have found a limited application in baking Japans.

The resinates have been extensively investigated. The preparation of lime and zinc resinates as a means of hardening rosin is discussed in the section on Hardened Rosin.

The resinate and stearate of lime have been used in powdered form for waterproofing cement and concrete or aggregate.

Two methods, fusion and precipitation, are employed in making metallic soaps. The fusion method is very simply carried out by heating the fatty acid or rosin to a temperature well above the melting point and adding a metallic oxide or decomposable salt, e.g., an acetate. Reaction takes place with much foaming and a soap containing a considerable amount of free fatty acid or rosin acid is soon obtained. The method is a cheap one but does not furnish as good a grade of product as the precipitation method.

The author has found the highest content of combined metal is secured in the fusion process, when metallic hydrates, freshly precipitated and not too strongly dried but retaining a voluminous form,

are added in portions to the molten fatty acid or resin, meanwhile stirring constantly to minimize the foaming. In no case, however, is it to be expected that a content of combined metal equal to that yielded by the precipitation process will result.

Precipitation Method.

This procedure, as the name implies, is that of treating an aqueous solution of ordinary soda or potash soap or the palmitates, oleates, stearates or resinates with a water-soluble metallic salt, thus to precipitate the corresponding water-insoluble metallic compound. The precipitated, unlike the fused, compounds contain a fairly definite percentage of combined metal.

Rosin is looked upon as essentially the anhydride of abietic acid and Steele¹² has developed a method for the conversion of rosin into abietic acid based on hydration of rosin with 98 per cent acetic acid. For the investigator in the field of preparing resinates the work of Steele is of interest.

Steele by means of the following experiments showed that rosin is hydrated by the action of a solvent containing water. In two flasks equal weights of rosin were dissolved by heating in approximately the same weight of 98 per cent acetic acid. One flask was then set aside while the contents of the other flask were boiled vigorously under a reflux condenser for 2 hours. The contents of both flasks were then brought to room temperature and a few crystals of abietic acid added to each flask. In a short time crystallization started in the flask which had been heated for the period of 2 hours, and after several hours this flask was nearly filled with crystals. The contents of the other flask did not crystallize to an appreciable extent, even after standing for 3 days. It was evident that the rosin was hydrated by heating with the 98 per cent acetic acid. The following method for the preparation of abietic acid from rosin was developed after a series of experiments.

Seven hundred grams of white rosin (WW or WG grade) in small lumps¹³ was boiled with 500 cc. of 98 per cent acetic acid for 2 hours under a reflux condenser. The mixture was then filtered while hot through a large plaited filter paper and the filtrate cooled to room temperature or lower. A few crystals of abietic acid were added to start crystallization or, when none of this product was available, the solution was allowed to stand overnight, whereby spontaneous crystallization took place. If the solution was "seeded" with abietic acid, it usually started to crystallize within an hour and the liquid became a solid mass of crystals after standing overnight. The product was filtered on a Büchner funnel with suction and the filtrate set aside for a second crop of crystals. The material on the filter was sucked as free from mother liquor as possible and washed with successive portions of cold alcohol (9 parts by volume 95 per cent ethyl or denatured alcohol to one part of water) until the filtrate was practically colorless.

The yield of air-dried product was usually about 350 grams counting the second crop of crystals recovered from the mother liquor. Some of the product, prepared as above, was placed on a bit of porous porcelain plate and washed with a little strong alcohol. This material when dried and powdered showed a melting point of 155-159° C. Some of the product was recrystallized from 95 per cent alcohol and then was found to melt at 158-162° C. These crystals had been washed thoroughly with the dilute alcohol and dried in a

¹² J. Am. Chem. Soc. 1922, 1333.

¹³ Rosin which has stood in powdered form for considerable lengths of time becomes partially oxidized and is unsuitable.

vacuum before the melting point determination was made. A material of melting point 161-165° C. resulted from a second crystallization in the same manner, while after a third crystallization, the product was unchanged in melting point.¹⁴

Steele used the following procedure in preparing metallic abietates from abietic acid. Freshly recrystallized acid was dissolved in about ten times its weight of denatured alcohol and nearly neutralized by the addition of a calculated amount of strong sodium hydroxide solution of known strength. The solution was then titrated to a faint pink color with dilute alcoholic sodium hydroxide solution, using phenolphthalein as an indicator. This neutral abietate solution was then poured slowly, with stirring, into a solution of a salt of the desired metal dissolved in forty to fifty times its weight of distilled water. A 50 per cent excess of the metallic salt was used in order to ensure complete precipitation of the abietate. The resulting soap was thrown down as an amorphous, more or less flocculent precipitate, which was filtered on a Büchner funnel and washed thoroughly with water until free from soluble material. In cases where the product formed a gelatinous cake on the filter, it was found advantageous to transfer it to a dish and churn it with water. This mixture was then filtered again on the same funnel.

The thoroughly washed product was dried in small portions in a vacuum in order to avoid oxidation. The wet precipitate was placed in a heavy-walled test-tube and connected with an oil vacuum pump, with a drying tower of fused calcium chloride between the tube and the pump. In order to hasten the drying, the tube was placed in a water-bath at 80 to 90°, whereby the greater part of the moisture was rapidly removed. The last traces of water were held rather tenaciously by the metallic soap and several hours were found to be necessary for complete drying of the product.

When the metallic abietates had been partially dried, the vaporization of the remaining moisture caused the particles to fly about violently, and a wad of absorbent cotton was necessary in the mouth of the tube to prevent loss.

The metallic content of the following abietates was determined.

Lead Abietate, calculated lead content 25.59, found 24.69

Manganese calculated 8.35, found 8.17

Cobalt calculated 8.91, found 8.44

Nickel calculated 8.87, found 8.04

Chromium calculated 5.44, found 14.93

Iron calculated 5.82, found 2.44

The conclusion is drawn that neither the iron nor the chromium abietate corresponds to a normal salt. All of the abietates examined by Steele with the exception of the chromium compound were soluble in benzol.

Acetate of Lime.

The calcium salts of volatile organic acids are looked upon favorably as hardening agents when a very light colored hardened rosin is required. Using acetate of lime, Bottler recommends 25-30 per cent, of the weight of the rosin, be employed. The batch is heated at 160° C. until acetic acid ceases to be evolved. Moist blue litmus paper held over the fusion kettle will serve to indicate the completion of the reaction. Although having the possible advantage of affording a lighter colored rosin, the use of this amount of acetate of lime adds considerably to the cost, over the customary procedure with hydrated lime.¹⁵

¹⁴ There is good evidence that abietic acid commences to form the anhydride at temperatures near its melting point and hence the observed melting point is not sharp.

¹⁵ *Kunststoffe*, 1913, 3, 84.

Banner¹⁶ claims that carbonate of lime, and calcium sulphide can be used to harden resin by employing a somewhat higher temperature than usual. Three per cent and upwards of sulphur and hydrated lime may be used.

Hardening with Oxygen.

Oxidation, as a means of hardening rosin, is employed by Schaal.¹⁷ Rosin is powdered and exposed to a current of heated air, the temperature being kept below the melting point of the material. The product is not readily soluble in spirits of turpentine and like fossil resins requires strong heating above its melting point to become soluble.¹⁸ Oxidation in other ways is obtained by Plauson.¹⁹ Turpentine, or crude rosin, is heated with a ferric salt in the presence or absence of hypochlorites, and the product is washed with water until all soluble constituents are removed. A tougher and less brittle resin is obtained by passing air or oxygen through a molten mixture of the product with 1 to 5 per cent of a monohydric or polyhydric phenol or phenol ester. Miles²⁰ calls attention to the very slow rate at which dry powdered rosin oxidizes on exposure to air. He believes this slow rate of oxidation is due to a film of inert gas on the rosin surface which protects the particles from access of fresh oxygen. Miles finds a better rate of oxidation to be obtained if the surface of the particles is rendered wet by water. In one case he agitates the powdered resin with an aqueous solution of hydrogen peroxide. In another case ozone is used as an oxidizing agent. The claim is made that a more rapid and uniform oxidation is effected. Rosin heated to 135° C. and blown with moist air, then with dry air at 140° C. acquires improved electrical insulating qualities.²¹ Ruth and Asser²² obtained from rosin oil products adaptable for use in varnish manufacture. A grade of oil of boiling point 200° C. or higher is treated under a reflux condenser with a current of air containing 10 to 15 per cent of highly-superheated steam until it becomes solid or nearly solid. The product on distillation yields 20 to 30 per cent of unchanged oil, 30 to 40 per cent of heavy resin oil and 30 to 40 per cent of black pitch. Bedford and Bedford²³ oxidize rosin oil with the addition of driers, using a special apparatus.²⁴ On protracted oxidation the oil becomes a viscous mass, and is proposed as a resin substitute in linoleum manufacture.²⁵

¹⁶ J. S. C. I. 1888, 573; British Pat. 11,805, Aug. 31, 1887.

¹⁷ U. S. Pat. 698,741, Apr. 29, 1902.

¹⁸ Note also Fahrion, *Zeits. f. ang. Chem.* 1907, 356; *Chem. Revue* 1911, 239; Schuckert, J. S. C. I. 1901, 729; British Pat. 7625, 1901.

¹⁹ German Pat. 346,308, May 6, 1920; J. S. C. I. 1922, 41, 261A.

²⁰ U. S. Pat. 1,410,211, Mar. 21, 1922.

²¹ Whipple, U. S. Pat. 1,083,168-9-10, Dec. 30, 1913.

²² German Pat. 336,253, May 9, 1920; J. S. C. I. 1921, 595A.

²³ J. S. C. I. 1898, 1158; British Pat. 29,656, Dec. 15, 1897.

²⁴ British Pat. 7742, 1893; J. S. C. I., 1893, 406.

²⁵ For a description of Fry's process of oxidizing rosin and oil of turpentine by nitric acid see Chapter 20, Nitro Resins. Rosin which has been oxidized by nitric acid has been recommended for use in making violin varnishes.

Formaldehyde Hardening.

Low²⁶ treats rosin with formaldehyde under a pressure of 75-150 lbs. the temperature ranging between 250° and 400° F. (121-205° C.), the best operating temperature being 250-300° F. (121-149° C.) and the treatment maintained for two hours or longer. The rosin is hardened and becomes more resistant to oxidation. Manila copal and gum dammar may be treated in a similar manner. Heating under pressure with an aqueous suspension of sulphur or with hydrogen peroxide also improves these resins.²⁷

Lime Setting Process.

Acid resins which react with a basic substance such as hydrated lime may be employed in compositions for molding. An ideal molding compound from the standpoint of cheapness is a mixture of rosin, hydrated lime and a fibrous filler to lend strength. A mixture of this nature has been prepared by the author and found to harden under hot pressing. However, the resin ate of lime formed by the heat treatment is not a serviceable binding agent. An excess of lime is required to secure rapidity of hardening and the heat-set binder proves too friable or so deficient in binding strength to have any but a limited application. The oxides or hydroxides of zinc, magnesium and barium behave similarly. The corresponding carbonates react very sluggishly. The substitution of shellac for rosin increases the strength but the product is no longer attractive on the score of cheapness. Tazewell²⁸ dissolves shellac in pine tar creosote, adds a filler and just before molding, enough of the hot mixture to fill the mold is incorporated with hydrated lime. Molding must then be carried out quickly or the mass will set prematurely. Barringer²⁹ adds zinc oxide or hydrated lime to a sulphurized oil and a filler. After molding, the articles are baked. (For details see Chap. 19.) Hardened rosin in conjunction with shellac occasionally is used in the production of abrasive articles and grinding wheels. A mixture of abrasive grains, shellac, rosin and a base, e.g., the oxides of calcium, zinc or lead is baked engendering hardening in part due to the formation of resinates.³⁰

²⁶ U. S. Pat. 1,243,312, Oct. 16, 1917.

²⁷ Lingner, German Pat. 203,847, Oct. 6, 1904; Chem. Centr. 1907, i. 1560, employs a process for producing solid, high melting condensation products in which the resin acids other than those of copaiba balsam are treated with formaldehyde in acid solution. The products serve for the formation of lakes.

²⁸ U. S. Pat. 1,190,815, July 11, 1916.

²⁹ U. S. Pats. 1,085,102, Jan. 27, 1914, and 1,111,430, Sept. 22, 1914.

³⁰ Lime-treated resins have been used as a cement for tools, Cefka-Ges. m. b. H., Chem. Abs. 1916, 10, 396; German Pat. 284,701, 1913.

Chapter 16.

Ester Gums or Artificial Resin Esters. Spar Varnishes.

Another and more important advance in the neutralization of acid resins is found in the application of glycerol (glycerine) as an esterifying agent. The situation in the preceding chapter relating to the frequent necessity of neutralizing acid resins with lime or other bases applies with equal force to resin esters or ester gums. In passing, we may note that these terms are employed by the varnish manufacturer to signify principally the compounds of the natural resins with glycerol. Simply by heating a mixture of rosin or acid resin with glycerol enables the acidity to be reduced to a marked degree through union of the two substances and the elimination of the water formed by the reaction. Thus the acid number of rosin, approximately 160, will drop to 10 or less on heating rosin with 10-12 per cent of glycerol. Rosin esterified in this manner not only is free from the objectionable property of livering with basic pigments exhibited by the raw rosin but the hardness and resistance of the resin to exposure to the weather is substantially improved.

Spar Varnish.

Ester gums to a large extent have displaced the copal gums in the manufacture of spar varnishes. A rosin ester Chinese wood oil varnish is notably waterproof and even will resist the action of hot water for a considerable period. The discovery of the valuable properties of the combination of ester gums and Chinese wood oil has created a noteworthy change in varnish making. In fact, specifications for spar varnishes have been modified in numerous instances in order to secure an ester gum varnish in preference to one made with hard fossil resins.¹

¹ Note recommended specification for Water-Resisting Spar Varnish, Circular 103, Second Ed., Bureau of Standards; J. Franklin Inst. 1922, 107; Circular 117, Bureau of Standards; Report of Some Results Obtained on Varnishes, Enamels and Pigmented Dope in Airplane Construction During 1917-1918, War Department, General Laboratories, Bureau of Aircraft Production; Signal Corps, United States Army, Specification for Spar Varnish for Use in Airplane Construction.

Glycerol (Glycerine).

Of all organic neutralizing agents which have been proposed, glycerol is by far the most useful. It is readily available and may be subjected to a high temperature without carbonization. Owing to its high boiling point, 290° C. (554° F.) a mixture of rosin and glycerol may be raised far above the boiling point of water. As esterification involves the formation of water and its removal, the operation should be conducted at a high temperature and, for most rapid results, under diminished atmospheric pressure.

Other Esterifying Agents.

The literature on the subject of resin esterification contains frequent reference to the use of carbohydrates as esterifying agents. Practically speaking, sugar, glucose, starch or similar carbohydrates are not used. They carbonize at too low a temperature and the discolored product is worthless for most varnish purposes. The reduction in acid number through such additions is negligible and the discoloration objectionable. On the other hand fair results may be obtained from glycol which has been suggested as an esterifying medium. Ordinary glycol boils at 197° C. (386° F.) or much lower than glycerol (290° C. or 554° F.) and the lower boiling point of glycol renders esterification more difficult because of volatilization. In one process of making glycol, the substance chlorhydrin is used as the raw material. The author has found boiling chlorhydrin to react with rosin, causing a considerable reduction in the acid number of the resin. For example, 2 parts by weight of rosin were heated with 1 part of chlorhydrin at the boiling point of the mixture for two hours under a reflux condenser. (The chlorhydrin was obtained by treating oil gas with hypochlorous acid and was a mixture of the ethylene and propylene chlorhydrins.) This treatment reduced the original acid number from its original point of 161 down to 113. On boiling for a further period of 8 hours and then distilling to remove the excess of the reagent, the acid number of the resin was 57. The resin obtained in this manner was easily soluble in alcohol and was light in color.²

It was found that under ordinary conditions ethyl alcohol, phenol, cresol, aniline and alpha and beta naphthylamine did not react with the rosin to form neutral products. Benzyl alcohol proved more reactive. Experiments carried out with sugar, glucose and starch under pressure in the presence of a water-absorbing adjacent layer of unslaked lime similarly gave negative results. For example, 100 parts of rosin and 15 parts of crystallized dextrose reduced to a fine powder and intimately mixed were placed in an open container surrounded by unslaked lime and heated in an autoclave at 253° C. (487° F.) for three hours. The pressure did not rise above three atmospheres. The final product consisted of unchanged rosin, the acid number of which was 145.6,

² Ellis and Weber, U. S. Pat. 1,381,863, June 14, 1921.

Chapter 16.

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the melting point of the rosin to a point where it approaches that of the copals. This product may then be esterified with glycerol, glucose, levulose or cane sugar.

Glycerol esters which can be immediately employed in the varnish industry are prepared according to Bottler⁸ by heating abietic acid to 180-210° C. (356-410° F.) in vacuo and adding to it 10 to 16 parts of glycerol under constant stirring. After the addition of the glycerol the temperature is gradually raised to 280° C. (536° F.) while the vacuum is maintained constant. The operation is continued until the esterification is complete. In order to impart to the ester a greater degree of hardness, the softer portions are distilled off under

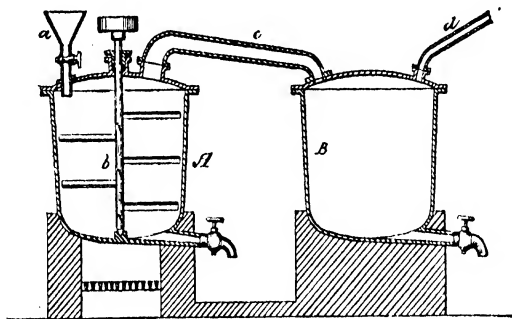


FIG. 10.—Schaal's Apparatus.

reduced pressure or in an atmosphere of an indifferent gas at ordinary pressure. If the product becomes very thick toward the end of the operation some linseed oil may be added. Finally, the residue is treated with $\frac{1}{2}$ to 2 per cent of manganese peroxide or red lead and the heating is continued until the solution is complete. The varnish stock thus obtained is of a light color and is readily soluble in benzene and turpentine.

Suter⁹ claims that he was able to bring about combination between dehydrated molasses and rosin in the presence of asphalt oil dissolved in a vehicle such as alcohol or turpentine. For example, 30 lbs. of copal and 20 lbs. of rosin are supposedly combined with 25 lbs. of molasses and 5 lbs. of asphalt distillate.

Various Experimental Procedures.

Investigations were carried out in the laboratory of the author¹⁰ with the object of finding a simple and at the same time an efficient method for producing substantially neutral rosin or other resinous compounds that would resist the action of basic pigments, such as white lead and zinc oxide. To be of commercial value these resinous products are required to possess not only a low acid number but good color and hardness as well. This offers difficulties as it is not easy, for instance, to obtain an ester possessing both a low acid number and

⁸ See also J. S. C. I. 1901, 263; British Pat. 4615, Mar. 10, 1900.

⁹ "Harze und Harzeindustrie," Hanover, 1907.

¹⁰ U. S. Pat. 905,384, Dec. 1, 1908.

¹¹ J. Ind. Eng. Chem. 1916, 406.

a good color. Either one or the other property has to be sacrificed in a measure unless special and expensive precautions are taken. To some extent the same is true of color and hardness.

Gas Currents.

Partial esterification of rosin by means of glycerol readily took place by bubbling gases¹¹ through a mixture of rosin and glycerol (in slight excess) at 280-300° C. (536-572° F.). Hydrochloric acid gas, carbon dioxide, hydrogen, air and oxygen were successively tested. Esters of very low acid number were not obtained.¹² For example, 50 parts of rosin and 5 to 8 parts by weight of glycerol were heated to 285° C. (545° F.) for two hours while a current of hydrochloric acid gas was passed through the molten mass. In this way, the acid number of the resulting product was found to be reduced to 1/15 of its original value and no hydrochloric acid was detectable in the finished product. The color was approximately that of the original rosin. The acid number of rosin was greatly lowered by heating to 290° C. (554° F.) glycerol and rosin and passing carbon dioxide through the mixture for 1¼ hours. The color was very good. A difficulty encountered in the use of these gases was the considerable loss of glycerol carried over by the gaseous current. A rosin ester obtained by the use of hydrochloric acid was of almost a semi-fluid consistency, while the esters prepared by the use of air or oxygen were generally dark in color. The use of bodies expected to aid the reaction by catalytic or dehydrating effect, such as sulphuric acid, zinc chloride and sodium acid sulphate, in the presence of gas, did not materially assist the ester formation.¹³ With the exception of hydrochloric acid gas, the action of the gases in bringing about partial esterification of the rosin is probably largely a mechanical one, as on bubbling through the melted rosin and glycerol, the gas brings these two substances into intimate contact. On the other hand, as already stated, the passing gas also causes considerable loss of glycerol. This accounts for the observation that only partial esterification takes place when using approximately equivalent amounts of rosin and glycerol under these conditions.

¹¹ Note U. S. Pat. 1,226,670, May 22, 1917; J. S. C. I. 1917, 894.

¹² To determine the acid number of rosin esters, one gram of the ester is dissolved in 25 cc. of benzol or ether and the solution is titrated with N/10 alcoholic caustic potash, using phenolphthalein as an indicator. Or, the acid number may be determined by dissolving 1 gram of the rosin ester in a mixture of benzol 50 parts and alcohol 50 parts and titrating with aqueous alkali. Care must be taken, however, that the solution contain at least 40 per cent of alcohol at the conclusion of the titration as aqueous solutions containing less alcohol rapidly hydrolyze the rosin soap. Lewkowitsch, *Chemical Technology and Analysis of Oils, Fats and Waxes*, 5th Ed., London, 1913, 437.

¹³ According to Hibbert (J. Am. Chem. Soc. 1915, 1748; U. S. Pat. 1,126,467, Jan. 26, 1915) the condensation of polyhydric alcohols is facilitated by the presence of iodine. Tests carried out on the rate of formation of the rosin ester of glycerol in the presence of small quantities of iodine did not disclose any beneficial result.

Mechanical Agitation.

A considerable improvement in the preparation of rosin esters was made by the introduction of a mechanical stirring device. This afforded the agitating effect of the gases without the drawback of excessive volatilization of glycerol. To reduce further the loss of glycerol a reflux condenser was used. This was arranged so that only the higher boiling constituents of the vapors were condensed and returned to the reaction vessel. Products were obtained in some of the tests having an acid number as low as 6 or 7. Murray¹⁴ does not consider mechanical agitation necessary as the reaction mixture is agitated by the escaping steam. The author, however, advises the use of a closed kettle equipped with an agitator, if large quantities of ester gums are to be made. See Figure 11, page 279.

Color of the Ester.

The production of rosin esters meeting the requirements of varnish manufacture as regards lightness of color is a matter of some difficulty, as the resin discolors rather rapidly when exposed to air or oxygen at the high temperature required for esterification. In consequence it is desirable to maintain an atmosphere of an inert gas over the esterifying material during the progress of the reaction and while cooling. Once an ester has become discolored by oxidation it is extremely difficult to better the color by bleaching operations. Small scale experiments carried out to determine the effect of various bleaching agents such as bone-black, fuller's earth and sulphur dioxide showed the coloring matter of the ester to be practically unaffected by these agents.

An ester gum made from a good grade of rosin and glycerol, when properly prepared, should have a light amber or pale straw color, should be bright and clear, with freedom from tackiness. It should not contain an excess of glycerol, and should dissolve readily in benzol or turpentine. A solution of equal parts of the latter and the ester gum should remain clear on standing. Rosin ester is practically insoluble in 80 per cent alcohol and should be substantially unaffected by 10 per cent solution of sodium carbonate. Boiling in water or even boiling aqueous solutions of sodium carbonate should have little or no immediate effect. The ester gum should be free from burnt or tarry odor.

Murray¹⁵ makes mention of resin esters on the market, some of which are very pale in color and are said to have been vacuum-distilled. It has been found that certain of these darken readily when cooked and that the resulting varnish is not lighter than that prepared from esters made in the varnish kettle.

¹⁴ Chem. Met. Eng. 1921, 25, 475.

¹⁵ *Ibid.*

Proportion of Glycerol.

The relatively higher cost of glycerol calls for the use of the latter in minimum amount. Esterification should be directed to the production of glycerol tri-resinate. The monoglyceride requires somewhat over 30 parts by weight of glycerol to 100 parts of rosin. The diglyceride requires about 15 parts of glycerol and the triglyceride slightly over 10 parts of glycerol. Although 10 per cent of glycerol based on the weight of the rosin is required by theory, not infrequently higher proportions, even as great as 20 per cent, are used in practice. Free glycerol is undesirable in a varnish as it lowers the resistance to moisture and tends to cause deterioration of the varnish film particularly when exposed to the weather.

Optimum Temperature.

Murray¹⁶ carried out a series of experiments to determine the optimum conditions for esterification. When glycerol is added to melted rosin at 150° C. (302° F.) combination immediately begins with foaming of the mixture. Although the fused material may be clear in appearance, drops removed and cooled will be turbid. The acid number decreases rapidly but heating at 150-250° C. (302-482° F.) for hours does not accomplish a high degree of neutralization of the rosin irrespective of the excess of glycerol present. However, when the temperature is raised to 290° C. (554° F.) which is the boiling point of glycerol, the greater portion of the rosin which previously resisted esterification will combine and a nearly neutral ester will result. To prevent excessive discoloration it is necessary to keep the mixture covered during esterification and loss of glycerol which is readily carried off by the water vapor is reduced. Murray does not recommend the use of a condenser as the steam must be permitted to escape. The author has obtained good results with an air condenser of such length that the steam will escape while glycerol for the most part is returned to the kettle. Proceeding in this manner the result is a glycerol tri-resinate which when carefully prepared will have an acid number of 5 or less. Murray notes that the ester will possess a somewhat lower melting point than the original rosin and will be slightly more tacky. This is not in concord with observations made by the author, a well-esterified product being less tacky than raw rosin if entirely free from uncombined glycerol.

Time of Esterification.

In some experiments made by Murray it was found that, esterifying at 555° F. (290° C.), the reaction passed through a peak about 15 minutes after this temperature was reached. Working with 12 pounds of glycerol per 100 pounds of rosin an ester with an acid number of 5 to 10 was secured in that time. However, if the heating

¹⁶ Chem. Met. Eng. 1921, 25, 475.

was continued there resulted a gradual increase in acidity which Murray attributes to the subsequent decomposition of the ester. There exists an analogy in this respect to the changes taking place in other glycerol esters. Linseed oil, for example, will decompose under prolonged heating with an increase in free fatty acid. Hence it is desirable that the varnish-maker conduct tests adequate to determine the peak of esterification and stop cooking at that point. Murray recommends avoiding the use of a sufficient excess of glycerol to neutralize the rosin completely and to complete the neutralization by the addition of lime. Thus he suggests employing 12 pounds of glycerol to 100 pounds of rosin and when esterification has reached the maximum point stir in a half pound of lime and remove the kettle from the fire. The resulting ester will be practically neutral and the small amount of lime contained will act beneficially as a hardening agent. His complete procedure is illustrated by the following example: Melt 600 pounds of rosin in a copper or aluminum kettle and when the temperature reaches 400° F. (204° C.) slowly add 72 pounds of glycerol, stirring being unnecessary as the mixture is strongly agitated by the escaping steam. Raise the temperature to 550° F. (290° C.) and hold at that point for about 20 minutes or for the period that is found to give maximum esterification. Then stir in 3 pounds of lime, remove the kettle from the fire and ladle the ester into cooling pans.¹⁷

Tunga Resin.

Gardner and Coleman¹⁸ have studied the formation of esters of rosin particularly in the presence of Chinese wood oil or tung oil and they apply the name Tunga Resin to the mixture of rosin esters and tung oil obtained by heat treatment. Gardner and Coleman found the presence of lime or lime soap to be beneficial in accelerating the reaction between glycerol and rosin. Methods of making rosin esters involving treatment of rosin with glycerol in the presence of resinate of lime have previously been proposed by Ellis and Weber.¹⁹ Besides quick lime, calcium cyanamide, barium and magnesium oxides also have been used. Ellis and Weber heated 200 parts by weight of rosin with 10 parts of calcium cyanamide for one-half hour and then treated the

¹⁷ When rosin and linseed oil are heated together to 300° C. (572° F.) the free fatty acid content remains about the same as that existing in the original fatty oil. Thus Ragg, *Farben-Zeit.*, 1921, 26, 2335; *J. S. C. I.* 1921, 552A, concludes that no glycerol-rosin ester is formed at the expense of the fatty acid glyceride. On dissolving 40 g. of crystallized lead acetate in 100 g. of rosin at 110° C., 133 g. of reaction product completely soluble in benzol is obtained. Since lead acetate is insoluble in benzol and the loss in weight accounts merely for loss of the water of crystallization, the formation of a definite compound of "acetoabietic acid" is suggested. The slow-drying properties of linseed oil and rosin or linseed oil and soft gum-resin preparations may be explained, according to Ragg, by the formation of similar complexes of the fatty and resin acids having properties different from those of the constituents.

¹⁸ Special Circular 101, Issued Aug., 1920, Paint Mfrs. Assoc.

¹⁹ U. S. Pat. 1,381,863, June 14, 1921.

product with 16 parts of glycerol for one-half hour at a temperature between 270-290° C. (518-554° F.). This afforded an ester having an acid number of about 5.²⁰

Gardner and Coleman also find the fume loss of rosin is reduced by the presence of lime during esterification. The results obtained by them check closely with observations made in factory practice. The presence of tung oil appears to favor esterification and calcium tungstate is apparently slightly more effective in accelerating the reaction than

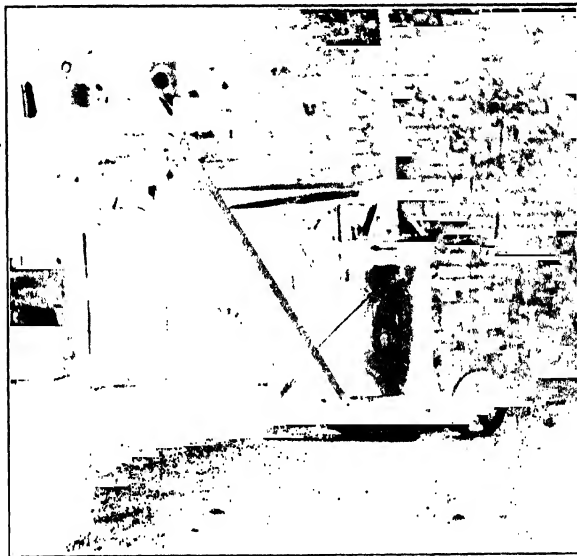


FIG. 11.—In experimental work conducted by the author on the esterification of rosin and copal resins the apparatus shown above was used. This consisted of an aluminum kettle fitted with a tight cover and stirrer mounted on a varnish kettle truck carrying a countershaft. The stirring device was operated by a motor. The kettle could be readily moved on and off the fire without affecting the operation of the stirrer. The apparatus proved very convenient to handle.

the resinate. When rosin is heated with glycerol and tung oil the exact manner in which the glycerol distributes is not known. The combination in the main is probably with the rosin but some reaction may occur with tung oil, forming the mono or diglycerides of the latter. The presence of lime soaps favors the combination of glycerol with rosin. In the absence of lime soaps Gardner and Coleman note

²⁰ *Lime and Glycerol*. A method recommended by Franke, *Farben Z.* 1910, 219, and Bottler, *Kunststoffe*, 1913, 3, 84, is to mix quicklime (from marble) in powdered form with warm glycerol. This mixture is added to molten rosin, with stirring.

the combination of glycerol tends to be initially with the tung oil rather than with the rosin.

The following methods of making varnishes from rosin and tung oil are offered by Gardner and Coleman:²¹

Waterproof Spar Varnish.

Rosin	100 parts
Glycerol	20 parts
Lime	6 parts
Chinese Wood or Tung Oil.....	240 parts
Manganese Tungate Paste Drier.....	14 parts
Lead Tungate Paste Drier.....	8 parts
Turpentine	60 parts
Mineral Spirits	300 parts

The proportions given above are by weight. The method of incorporation is to melt the rosin with 25 parts of tung oil employing a temperature of 350° F. (177° C.). The lime is added and thoroughly stirred into the mixture and the temperature is raised to 500° F. (260° C.), in order to dissolve the lime and bring about a partial polymerization of the tung oil. Then the temperature is dropped to 350° F. and the glycerol is added. Again the temperature is raised to 500° F. and is held at that point for about 1 hour. The remainder of the tung oil is added slowly while keeping the temperature of the batch at 450° F. (232° C.) or higher while the oil is being introduced. The precaution should be taken of adding the tung oil slowly and to avoid a drop in temperature much below 450° F. as the ester may be thrown out of solution and is redissolved with difficulty. The driers are added at 450° F. and the temperature held at this point in order to body the oil. This step may require from one-half to one hour. A sample (pill) should be stiff but not gelatinous or stringy. When the requisite body is obtained the batch is cooled somewhat and thinners added at 350-400° F. (177-204° C.). If given an extremely heavy body a larger proportion of thinner will be required. The turpentine may be replaced, at least to a very large extent by mineral spirits. In thinning the turpentine should be added first followed by the mineral spirits. A varnish of this character prepared by Gardner and Coleman dried hard in 5 hours giving a flexible coating and a panel varnished with the composition showed no whitening or softening of the film on exposure to boiling water for 15 minutes. The acid value of the varnish was 5.37 (in alcohol and benzol).

Long Oil Varnish.

Rosin	100 parts
Glycerol	25 parts
Lime	8 parts
Tung Oil	400 parts
Manganese Tungate Drier.....	20 parts
Lead Tungate Drier.....	12 parts
Turpentine	125 parts
Mineral Spirits	450 parts

In this case the lime is added to the cold tung oil and the mixture heated to 350° F. (177° C.). At that temperature a lime soap forms and settles to the bottom of the kettle. When the oil layer becomes clear add the rosin and raise the temperature to approximately 400° F. (204° C.) at which point the soap will dissolve. The temperature then is allowed to fall to 350° F., the glycerol added and the temperature raised to 475° F. (246° C.). After 45 minutes heating at this temperature the driers are added at 450° F. (232° C.) and heat-

²¹ Special Circular 101, August, 1920, Paint Mfrs. Assoc.

ing at this temperature continued until the proper body is obtained. From 15 to 30 minutes may be required.

This varnish is of course slower drying, requiring about 10 hours to dry hard. A coated panel immersed in boiling water for 15 minutes exhibited only a very slight degree of whitening and no softening of the film. The acid value of the varnish (in alcohol and benzol) is 5.74.

Short Oil Varnish.

Rosin	100 parts
Glycerol	55 parts
Tung Oil	100 parts
Manganese Tungate Drier.....	10 parts
Lead Tungate Drier.....	6 parts
Turpentine	50 parts
Mineral Spirits	220 parts

The rosin and tung oil are melted together at 350° F. (177° C.) and the glycerol introduced. Then the temperature is raised to 475° F. (246° C.) and is maintained at that point for 45 minutes. The driers are added at 450° F. (232° C.) and appropriate body obtained by heating for about 45 minutes at that temperature.

A flexible varnish was obtained in this manner by Gardner²² and Coleman which dried hard in 10 hours and the coated panel withstood boiling water for 15 minutes without softening of the film and with only a very slight degree of whitening.

Zinc Catalyst.

Rosin esters of low acid number are obtained by Sterling, Grotlisch and Veitch²³ with the aid of a zinc catalyst. 150 parts of rosin, 20 parts of glycerol and 0.5 part of finely divided zinc were heated under a reflux condenser, air-cooled, to a temperature between 275-280° C. (527-536° F.) for one-half hour. The condenser then was removed and the temperature was raised to 310° C. (590° F.) to drive off any excess of glycerol. By this procedure an ester having an acid number of 0.9 was obtained. Zinc oxide and zinc carbonate acted in a manner similar to the metal. In another case 450 parts of rosin and 60 parts of glycerol were heated in a zinc-lined vessel under an air reflux condenser for one-half hour to approximately the same initial temperature. Then the temperature was raised to 310° C. (590° F.) and the product allowed to cool to 160° C. (320° F.) out of contact with the air. The acid number was 1.2. Without the addition of zinc or zinc compounds it was necessary to heat the mixture for 2 hours to obtain a product of similar acid number.^{23a}

²² The author wishes to take this opportunity of expressing his appreciation of the courtesy of Dr. H. A. Gardner in permitting extensive reference to be made in this chapter of the work of Dr. Gardner and his associates in the field of rosin esters and rosin tung oil varnishes.

²³ U. S. Pat. 1,395,874, Nov. 1, 1921.

^{23a} The conversion of organic acids, other than polyhydroxy-fatty acids, into esters is stated to be accelerated by the use of zinc or tin or other metal of the periodic group including tin. The metal need not necessarily be in the finely-divided state; it may be introduced into the apparatus in the form of a regulus or be applied to the floor or wall or to a body inserted in the vessel. Haddan, Zollinger-Jenny. British Pat. 183,897, April 4, 1921; J. S. C. I. 1922, 41, 786A.

282 SYNTHETIC RESINS AND THEIR PLASTICS

Varnish Containing Free Rosin.

A formula for the preparation of ester gum spar varnish used in one varnish plant is the following.

45 gal. Chinese wood or tung oil
5 gal. linseed oil
100 lbs. ester gum
50 lbs. rosin
1 lb. litharge
 $\frac{1}{4}$ lb. cobalt acetate

To which is added 50 per cent by volume of thinner composed of three parts by volume turpentine and one part heavy benzine or mineral spirits.

The tung oil may be raw or "prepared." The prepared oil is made by heating the raw oil to 400° F. (204° C.) for 1½ hours and allowing to settle to remove albuminous matter. The two oils of the above formula are heated together to 300° F. (149° C.) and the litharge added. The temperature is then raised to 450° F. (232° C.) and held at that point to body the oil. When the latter begins to thicken add the ester gum and rosin and heat to 600° F. (315° C.). To reach this temperature probably the kettle should not be heated to more than 580° F. (304° C.) and then pulled from the fire as the temperature will rise to about 600° F. (315° C.) after the kettle has been removed. When the temperature has fallen to about 450° F. (232° C.) add the cobalt acetate. At about 420° F. (215° C.) the thinners may be added. The use of a small proportion of linseed oil is considered desirable as the varnish is rendered more elastic thereby. The presence of the proportion of rosin indicated is reported not to materially detract from the waterproof qualities of the varnish and its presence apparently is useful in blending the several ingredients.

A process of rendering rosin and other resins resistant to water by treatment with certain halides of the substituted benzene series, such as benzyl chloride, to produce esters by reaction with the acids of the resins, has been devised by Crane.²⁴ These compounds are not spotted by water as is the case with ordinary rosin.

Dammar Ester.

Experiments made in the author's laboratory on dammar resin did not yield very satisfactory results owing to the darkening which occurred on esterification. In one case a mixture of 50 parts of dammar and 5 parts of glycerol was heated for one-half hour under agitation at 250° C. (482° F.). The acid number fell from 39 to 12.5. The final product was dark in color.

Esterification of Copal Resins.

The esterification of the copals involves a less simple procedure than that employed in esterifying ordinary rosin. The copals are normally insoluble and cannot be fused without running or cracking by protracted heating at high temperatures. Furthermore under some

²⁴Private communication from Dr. F. D. Crane, Montclair, N. J.

conditions the resin reacts with glycerol to an infusible product as will be later described. However, the esterification of fossil resins when properly conducted yields approximately neutral products of a hardness and toughness far surpassing those obtained by the esterification of rosin and in recent years considerable attention has been paid to the problem of obtaining light colored esters of congo and manilla gum and other copals. Also the addition of copal in small proportion to rosin and esterification of the mixture, after thoroughly cracking the copal, yields a harder and tougher resin than that obtainable from rosin alone. The fusing and cracking of copal is facilitated and esterification is advantageously conducted in the presence of ordinary rosin. The procedure has been described by Ellis and Weber²⁵ especially with reference to the production of mixed congo and rosin esters. 4 or 5 parts of congo gum and 1 or 2 parts of rosin are melted and heated to 300-310° C. (572-590° F.) for a period sufficient to convert the congo to a fusible product. Resinate of lime also may be present. Glycerol is added and esterification carried out at a temperature between 270-290° C. (518-554° F.). Murray^{25a} found the addition of 10 per cent of congo gum to rosin ester greatly improved the latter, adding considerable toughness and hardness. This addition was accomplished by heating the rosin and congo in a covered kettle at 600-610° F. (316-321° C.) until the congo was completely dissolved in the rosin. Glycerol should not be added until the melt is in an entirely fluid condition. After the congo was entirely melted the batch was cooled to 550° F. (288° C.) and 12 parts of glycerol added. The reaction with the glycerol was allowed to progress as in the case of the esterification of rosin alone until a product as nearly neutral as possible was obtained.²⁶

Terrisse²⁷ has esterified a variety of varnish gums with glycerol. Fossil resins are "solubilized"²⁸ by heating them, preferably under pressure in an autoclave at 240-360° C. (464-680° F.) with the addition of naphthalene or phenol. The naphthalene or phenol is removed by distillation, the acid value of the fused resin is determined, and an excess of glycerol is added. The mixture is then heated until the uncombined glycerol is distilled off, the product consisting substantially of a neutral resin acid ester, readily soluble in linseed oil. For example: (1) 100 g. of ground Zanzibar gum are heated with 350 g. of naphthalene at 280° C. (536° F.) at 4 atmospheres for 4 hours, or until a test portion is soluble in linseed oil. The acid value is determined, and some excess above the calculated amount of glycerol is

²⁵ U. S. Pat. 1,381,863, June 14, 1921.

^{25a} Chem. Met. Eng. 1921, 25, 475.

²⁶ Böttler, *Kunststoffe*, 1913, 3, 85, has observed that the esterification of rosin, congo and manilla copal is carried out almost exclusively with glycerol in special apparatus capacious enough to allow for much foaming. The glycerol is not used in excess.

²⁷ J. S. C. I. 1916, 57; British Pat. 23,055, Nov. 25, 1914; Chem. Abs. 1916, 440; U. S. Pat. 1,236,996, Aug. 14, 1917.

²⁸ J. S. C. I. 1904, 552; British Pat. 14,554, June 30, 1903.

added. The mass is then heated in a still or open vessel at 280-320° C. (536-608° F.) until a test on glass remains transparent on cooling. (2) 100 kilos of congo copal are fused by the open-kettle method; its acid value is then determined and the calculated amount of glycerol is added. 15 kilos of copal oil, redistilled under reduced pressure to the state of a greenish yellow viscous liquid, are added, and the mixture is heated in a still or an open vessel to 280° C. (536° F.); 5 to 6 kilos of glycerol are then added and heating continued until a test gives a clear bead.²⁹

Glycerol esters of the acids derived from fossil resins incorporated with linseed or tung oil are used by Terrisse³⁰ in making insulation varnish or paint. Enamels made from this composition and containing zinc oxide or other basic pigment do not liver. Coating compositions, containing resin esters, which are intended for use on concrete surfaces are proposed by Ellis.³¹ Rosin esters in conjunction with hard varnish resins and sulphured tung oil are employed by Hollenbeck and Horn³² in making varnishes. A solution of ester gum and ordinary rosin is used by Butterfield³³ for sizing and proofing textile fabrics. Scobel (see Chap. 23) employs ester gum in tung oil plastics.

Concerning the formation of mixed esters of glycerol with rosin and phthalic acid see Chap. 17.

Polymerization of Copal Esters.

Under some conditions copal resins when heated with glycerol solidify in the kettle to an infusible mass. During an investigation conducted in the author's laboratory this phenomenon was observed.³⁴ For example, congo resin was run at 327° C. (620° F.) until apparently sufficiently soluble in turpentine and glycerol then was added. A vigorous reaction occurred, yielding a spongy product which could not be fused even on heating to over 360° C. (700° F.). On cooling a porous resinous mass was obtained. Murray³⁵ observed a similar phenomenon and attributed it to the polymerizing action of the copper of the varnish kettle employed. He was studying the effect of adding congo resin to rosin during the esterification of the latter with glycerol and as the amount of congo increased in proportion to the rosin darkening took place accompanied by uncontrollable foaming, increasing with the amount of the hard gum used. When a proportion of two parts of congo to one part of rosin was reached the mass became very dark and solidified before the glycerol could be combined. This solidification occurred very rapidly at 290° C. (555° F.) and strik-

²⁹ See also Terrisse, *Chem. Umschau*, 26, 194; *Pharm. Zentrallh.* 1920, 171; *Olien en Vetten* 4, 660; *Chem. Abs.* 1920, 2720.

³⁰ U. S. Pat. 1,214,611, Feb. 6, 1917.

³¹ U. S. Pats. 1,189,550 and 1,189,551, July 4, 1916.

³² U. S. Pat. 1,190,765, July 11, 1916.

³³ British Pat. 168,174, June 8, 1920.

³⁴ J. Ind. Eng. Chem. 1916, 406.

³⁵ *Chem. Met. Eng.* 1921, 25, 475.

ingly resembled the polymerization of Chinese wood oil. Murray made several unsuccessful attempts to control the action in copper kettles and then repeated the experiment using an aluminum vessel with the result that foaming and darkening were negligible and the ester remained liquid until the end of the operation and could then be readily poured from the kettle. Using an aluminum vessel Murray found it possible to make esters with 3 parts of congo to one of rosin, using 10 pounds of glycerol to 100 pounds of the resins. The resulting ester exhibited a hardness approaching that of kauri and possessed an acid number of 7.5 or less. The ester was found very serviceable in the preparation of varnishes, paler in color than those which can be made from kauri. As a result of these experiments Murray was convinced that copper acts as a polymerization catalyst on congo copal during esterification.

Subsequently Gardner and Holdt³⁶ studied the conditions under which polymerization occurred, noting, for example, the following. Congo copal was heated quickly to 315° C. (600° F.) and held for about half an hour at approximately that temperature. At the end of this time the resin was completely melted and clear. It appeared to be sufficiently cracked. The temperature was dropped to about 280° C. (536° F.) and 10 per cent of glycerol was added. Then the temperature was raised to about 290° C. (554° F.) to bring about the combination of the resin acids and glycerol. After heating for about 30 minutes with the glycerol the mix suddenly became thick and gummy, then almost solid, swelling to such an extent as to almost completely fill the vessel. A spongy porous mass was obtained. As the reaction was carried out in a glass vessel, no copper being present, Gardner and Holdt sought to locate the cause of this change on other grounds than that offered by Murray. The resin alone could not be made to polymerize even after prolonged heating in the absence of glycerol, hence the change must be attributed to the presence of the latter.

The polymerization of manilla and pontianac copals was found to be very similar to that shown by congo. In each case the first indication that jelling was about to take place was a sudden foaming, very similar to, but much more violent than, the foaming which sometimes occurs when the resins are being melted. The liquid was observed to become very thick, the bubbles rising through it more and more slowly as the thickening progressed. Sometimes the entire liquid became a mass of foam that completely filled the vessel. In some cases polymerization took place very rapidly. In other cases it occurred more slowly. The speed of the reaction probably depends upon the degree of cracking of the resin. There are evidently substances in the uncracked resin which react with or combine with the glycerol to bring about this change. These substances appear to be altered in some way by sufficient preliminary heating, so that polymerization does not result. Further experiments by Gardner and Holdt showed

³⁶ Circ. 151, 270, Paint Mfrs. Assoc.

that polymerization would not occur if the resin is completely cracked previous to the addition of the glycerol. Congo copal heated for 1 hour and 30 minutes and then treated with 10 per cent of glycerol did not polymerize. The esterified material remained entirely liquid. The excess of glycerol in this case was considerable and on cooling was apparent in the solidified resin. A determination of the minimum time of heating to avoid polymerization was next made. When a period of 45 minutes for cracking was allowed polymerization began in 40 minutes after the addition of glycerol. On cracking the resin for a period of 1 hour polymerization began about an hour after the glycerol was introduced. On cracking for a period of 1 hour and 10 minutes no polymerization occurred after the addition of the glycerol. Thus Gardner and Holdt conclude that cracking must continue for more than an hour to prevent polymerization but that no definite time limit can be set as the intensity of heat, size of kettle and general factory practice will modify the conditions sufficiently so that the time of heating for each set of conditions should be established in all cases. Polymerization apparently takes place more quickly in copper than in glass, according to Gardner and Holdt, but attempts made by them to bring about polymerization of the thoroughly cracked resin in a glass flask in the presence of copper failed. The observations of Gardner and Holdt also indicate that aluminum influences polymerization. Cracking appears to be more easily completed in aluminum than in copper but if the cracking is not complete polymerization in aluminum is very rapid. In one observation this occurred almost immediately after the addition of glycerol.

Progress of Esterification.

Congo resin was cracked for $1\frac{1}{4}$ hours at $315\text{--}325^{\circ}\text{C}$. ($600\text{--}617^{\circ}\text{F}$.). It then showed an acidity of about 80. Six per cent of glycerol was added at 280°C . (536°F .). The following table shows the effect of the time of heating on the degree of esterification:

<i>Time of heating with glycerol</i>	<i>Observations</i>	<i>Acid value</i>
10 minutes.....	Much glycerol left uncombined. Product cloudy.	42
20 minutes.....	Some glycerol uncombined. Product somewhat cloudy.	36
30 minutes.....	Few drops of glycerol on side of flask at end of heating. Product clear.	30
40 minutes.....	Product clear.	23
50 minutes.....	Product clear.	19
60 minutes.....	Product clear.	15
2 hours.....	Product clear but very dark.	5.5

The above results show that esterification takes place rapidly at first and decreases in speed as the glycerol combines with the resin acids. The acid value, it will be noted, was reduced to almost one-half during the first 10 minutes. The rate of reaction is somewhat greater when an excess of glycerol is used. The period of heating may vary according to the extent of esterification desired and should be conducted long enough to drive off the excess of glycerol and insure a bright clear ester. Cloudiness due to uncombined glycerol or an excess of glycerol can be tested during the esterification operation by placing a few drops of the melt on a glass plate, allowing to cool and observing the clarity. As a result of numerous tests Gardner and Holdt offer the following procedure:

Bring the resin quickly to 315-325° C. (600-617° F.) and hold for 1¼ to 1½ hours or even longer according to factory practice and other conditions. Drop temperature to 280° C. (536° F.) and add glycerol in moderate excess (6 to 8 per cent). Raise temperature to 292-295° C. (about 560° F.) and hold until the desired degree of neutralization has been reached. The mass may then be cooled and poured into containers and stored. If, however, it is desired to continue the reaction for the production of a varnish, the cooked and processed oils may be added, and after sufficient heat treatment the mass may be thinned as usual.

Copal Esters Minimize Livering.

An experiment by Gardner and Holdt²⁷ showing the absence of livering when esterified copal is employed in varnishes is of significance. Varnish A made with esterified copal had an acid number of 4 while Varnish B gave an acid number of 25. On grinding with zinc oxide an immediate effect was noticed. The B formula required twice as much varnish as A to bring to working consistency. A noticeable thickening of B occurred in a few hours, in two weeks the mixture was thick and livery and in 8 months a stiff putty, almost solid. At the end of this time Sample A showed an unchanged consistency.

Resistance of Copal Esters to Alkali.

Run copal, esterified with glycerol, is far more resistant to alkali than the unesterified resin. Gardner and Holdt²⁸ exposed samples of these products to 4 per cent and 16 per cent solutions of caustic soda. After one week the samples which had been run but not esterified were badly affected, being covered with a thick white scum. The esterified samples were entirely unaffected in either solution. This increased resistance to alkali exhibited by esterified copals may be utilized in the production of soap-proof varnishes. In varnishes to be used on linoleum or oil cloth the presence of copal esters should be beneficial.

Chlorinated Resins.

Resinous bodies are produced by the protracted chlorination of various oils and balsams. Boehringer & Soehne²⁹ have obtained such products by the introduction of 30 per cent or more of chlorine into fats, oils, waxes, balsams and natural resins, petroleum, paraffin and montan wax. The substance to be chlorinated is dissolved in carbon

²⁷ Circ. 151, 277, Paint Mfrs. Assoc.

²⁸ Circ. 151, 278, Paint Mfrs. Assoc.

²⁹ German Pat. 256,856, Nov. 19, 1910, and 258,156, Dec. 28, 1911.

tetrachloride. A higher degree of chlorination is obtained through the aid of catalyzers,⁴⁰ iodine, chlor-iodine, and the chlorides of aluminum, iron, vanadium and cerium being recommended. Paraffin with more than 70 per cent of chlorine is a transparent solid. With a 60 per cent chlorine content, rosin has a softening point of 105° C. and a melting point of 115° C.

⁴⁰ German Pat. 275,165, March 17, 1912.

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Chlorinated Resins.

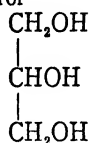
Resinous bodies are produced by the protracted chlorination of various oils and balsams. Boehringer & Soehne²⁹ have obtained such products by the introduction of 30 per cent or more of chlorine into fats, oils, waxes, balsams and natural resins, petroleum, paraffin and montan wax. The substance to be chlorinated is dissolved in carbon

²⁷ Circ. 151, 277, Paint Mfrs. Assoc.

²⁸ Circ. 151, 278, Paint Mfrs. Assoc.

²⁹ German Pat. 256,856, Nov. 19, 1910, and 258,156, Dec. 28, 1911.

with glycerol



With such an array of hydroxyl groups it is evident here that a considerable degree of condensation may be anticipated. In fact, for resinification the condensation must proceed to a stage sufficient to form a water-insoluble body and, of course, it is desirable that a still greater degree of condensation occur in order to yield a resin unaffected by water; that is, a product devoid of hygroscopic properties.

Glycerol and some of the organic acids derived from vegetable sources such as tartaric acid were available to chemists of earlier days and therefore it is not surprising to find Berzelius and other chemists of the period making observations on the reaction of these substances when heated. A soft mass was obtained by him from glycerol and tartaric acid on heating to 150° C. This could be drawn out into threads but was deliquescent and decomposed by water. The substance united with bases to form salts.

Succinic Acid.

A product termed succinin was obtained by Van Bemmelen on heating equal weights of succinic acid and glycerol to 130° C. More glycerol thus was present than corresponded to the acid equivalent. The product was a thick syrup which was heated further to 200-220° C. for several hours which caused the mass to become hard and tough, losing all acid taste. The resinous material was of a brownish black color, insoluble in water, alcohol, ether or carbon disulphide. When boiled with alcohol and water it slowly decomposed, forming a syrupy substance. The resin also dissolved on treatment with caustic alkali solutions or with a suspension of lead oxide.

Succinic and Benzoic Acids.

One equivalent each of succinic and benzoic acids and somewhat more than one equivalent of glycerol were heated. Water was driven off at about 100° C. and at 140° C. benzoic acid began to sublime. Additional quantities of benzoic acid were added and the mixture heated to 200° C. for several hours until benzoic acid no longer sublimed. When hot the product was a viscous black mass cooling to a tough elastic substance which could be drawn into threads. It was insoluble in alcohol, ether and water but decomposed slowly on boiling with water. It dissolved readily in hot alkaline solutions. Van Bemmelen¹ observed that the succinic acid combined quickly

¹ J. prakt. Chem. 1856, 69, 84.

with the glycerol while the benzoic acid combined subsequently and less readily. The product was termed benzo-succinin.²

Citric Acid.

Further experiments by Van Bemmelen on citric acid yielded a product which he termed citrin. One equivalent of citric acid in an excess of glycerol when heated at 160° C. yielded a syrupy product and after several hours heating at 160-170° C. a very hard tough brownish yellow porous substance resulted. It was hard to pulverize. Even at 200° C. the material exhibited approximately the same consistency as at room temperature. On exposure to air the sample grew softer. It proved to be insoluble in water, alcohol and ether and when allowed to stand in cold water for a long time no acid reaction was observed. When boiled with alcohol and water a thick syrup was obtained. One equivalent of citric acid with approximately two equivalents of glycerol heated for several hours to 170° C. yielded citro-diglycerol.

One equivalent each of citric acid and glycerol heated for 20 hours at 160° C. yielded a very hard light yellow transparent resin. This adhered tenaciously to the glass of the vessel in which it was prepared and could not be readily separated therefrom. It proved to be much harder than citro-diglycerol and did not soften in the air like the latter. In hot and cold water very little action was noticed. It was soluble in concentrated hydrochloric acid and dissolved in sulphuric acid with blackening. Van Bemmelen considers this product to be citro-mono-glycerol. Van Bemmelen summarizes the reaction between citric acid and glycerol in this manner: at 100-120° C. a syrup is formed and water is evolved, between 100-200° C. the syrup grows thicker and after some time, when from 4 to 6 equivalents of water have been evolved, a solid neutral insoluble substance is obtained.

Debus³ obtained a water-soluble syrup by heating to 170° C. equivalent proportions of succinic acid and mannite. Equivalent quantities of mannite and citric acid at 140° C. gave a hard yellowish, tasteless substance insoluble in water, alcohol and ether. Cane sugar and succinic acid at 160° C. yielded a humus-like substance.

Rosicki⁴ heated isosuccinic acid 1 part, resorcin 2 parts and sulphuric acid 1 part to 120-150° C. for 4 hours. On boiling with water brownish flocks remained which were soluble in alcohol, ether and alkalies. A red lacquer was produced containing lead.

Funaro and Danesi⁵ also prepared succinin according to Van Bemmelen's method. Succinic acid and glycerol were heated to 200° C. and the product dissolved in boiling water, boiled with animal charcoal and filtered. On cooling succinin separated as a colorless semi-solid mass.

² Kailan has studied the velocity of reaction between glycerol and benzoic acid, with and without catalyzers. *Rec. Trav. Chimie Pays-Bas*, 1922, 41, 592.

³ *Phil. Mag.* (4), 16, 438; *Ann. Ch. Pharm.* 109, 227; *Jahresber. Fort. Chem.* 1858, 435.

⁴ *Jahresber. Fort. Chem.* 1880, 799; *Ber.* 1880, 208.

⁵ *Gazz. chim. ital.* 10, 58; *Jahresber. Fort. Chem.* 1880, 799.

Lourenço⁶ heated citric acid and glycerol to 160° C. obtaining a gummy water soluble body. On heating to 215° C. a hard, brittle product, insoluble in water, was obtained.

Watson Smith's Resin.

In 1901 Watson Smith⁷ heated a mixture of glycerol and phthalic anhydride, in the proportions corresponding to diglyceryl triphthalate, for a long time nearly to boiling and on cooling a solid resin-like, perfectly transparent and strongly refractive substance was obtained. This substance was insoluble in water, but soluble in an excess of glycerol on heating. From the solution in glycerol, white oily drops separated on the addition of water, soluble in alcohol and ether. Similar resin-like masses were obtained using zinc chloride and these deliquesced and became sticky on exposure to air. Upon distilling in vacuo to remove the excess of glycerol a mass resembling glass slag was obtained. The end point of the distillation was noted when frothing set in. The same compound was obtained regardless whether an excess of phthalic anhydride or an excess of glycerol was used. The resin was easily saponified by means of alkali hydrates. Smith varied the fusibility of the resin by stopping the distillation of the glycerol in vacuo at some intermediate point. The melting point and the decomposition point were not far apart, the fusion point being at 190° C. and the decomposition and charring point at 220° C. At 220° C. the resin was not completely melted and crystals of phthalic anhydride were deposited on the sides of the tube. The resin ignited readily and burned with a bright flame but did not melt, only softening. Smith recommended it as a cement for glass and earthenware.

Arsem considers these resins to be complex esters. The fact that they may be resolved into alcohol and acid by an alkaline saponifying agent indicates this to be the case at least in the earlier stages of resinification. Probably a mixture of mono, di and tri esters form and these condense with each other to a greater or lesser degree. The activity of "polyglycerol" in contrast to glycerol, observed by Weisberg and Potter, particularly suggests the possibility of condensation between mono and di esters. The ultimate resinous product of condensation, which is insoluble, infusible and not easily attacked by alkalies, is looked upon as a cyclic body.

According to Weisberg⁸ the condensation of glycerol with polybasic acids takes place in three stages.

A. An initial condensation product which is soluble in acetone and is fusible. Its melting point seldom exceeds 120° C. This resin is not resistant to cold water but on further heating passes over into a resin of class B.

B. This resin is an intermediate condensation product insoluble in acetone and infusible, although it can be molded under heat and pressure. Like the resins of class A it is not resistant to cold water. On heat treatment it is converted into a resin of class C.

⁶ Ann. chim. phys. 1863, (3), 67, 313.

⁷ J. S. C. I. 1901, 20, 1075.

⁸ U. S. Pat. 1,413,145, Apr. 18, 1922.

C. This resin represents the final condensation product. It is insoluble in acetone and infusible; however, it can be molded under heat and pressure. The resin is resistant to both cold and boiling water. The resin produced from glycerol and phthalic acid is very brittle and the addition of an aliphatic acid tends to reduce brittleness, although probably diminishing resistance to water. In fact, a tougher and more elastic product is obtained when a substantial proportion of a dibasic aliphatic acid, e.g., succinic, malic, tartaric, maleic or fumaric acid is present.

Glyptal Resins.

The chemical staff of the General Electric Company has made a considerable study of resinous bodies produced from glycerol and organic acids and the name "glyptal" has been given to resins of this type. Thus far the commercial applications of glyptal resins are of a minor character.

A small amount of resin is made by reacting on glycerol with phthalic anhydride and oleic acid, which yields a rather tough and rubbery material, and is used on electrodes which come in contact with litharge. The latter has been found to affect linseed oil but does not destroy the glyptal coating. The phthalic-oleic glycerol resin is applied in acetone solution and when the coating is baked a surface is obtained which exhibits a greater degree of resistance to water than is shown by shellac. Undoubtedly resins of this general character have valuable properties but their development has been restricted by the high price of phthalic acid which is, as a matter of fact, the acid component generally employed as the essential acid constituent. Processes developed in recent years for the oxidation of naphthalene to form phthalic acid by passage with air over a heated catalyst may bring the price of phthalic acid and its anhydride to a point where a more extensive application of resins of the glyptal type may be expected. Very interesting resins have been obtained from fumaric and tartaric acids.

As a result of a series of investigations Callahan⁹ concluded that the organic acid should be used in excess of equal proportions; otherwise a soft sticky resin results. He recommends 2 parts of succinic acid or $1\frac{1}{2}$ parts citric acid to 1 part of glycerol. A greater proportion of acid renders the product too hard. For succinic acid the temperature of treatment is 220° C. and for citric acid 160° C. The time of heating depends somewhat on the size of the batch, from 15 minutes to 3 hours being required. Heating is continued until the resin is no longer sticky. A solution of the soluble resin in acetone may be used as a varnish. Callahan¹⁰ gives certain particulars of operation as follows:

One part by weight of glycerol and 2 parts of phthalic anhydride are heated slowly. At 100° C. the mixture forms a clear liquid and as the heating continues, distillation to a slight extent occurs. At 185° C. the temperature rise should be checked until distillation ceases. Then the heating is continued at a higher temperature, about 210° C., until the first stage of the reaction is completed. This degree of conversion is ascertained by withdrawing small samples, cooling and observing if these are hard and brittle without stickiness. The resin is yellowish and transparent.

⁹ U. S. Pat. 1,091,732, Mar. 31, 1914.

¹⁰ U. S. Pat. 1,108,329, Aug. 25, 1914.

Infusible Product.

If the heating is continued at 210° C. further change takes place with evolution of heat. At 275° C. a violent ebullition sets in and a brittle infusible mass filled with cavities is obtained. Even by holding the temperature at 210° C. vesiculation takes place.

Avoidance of Bubbles.

Callahan prevents vesiculation when carrying out the transformation or polymerization to an insoluble product by heating at 85-100° C. (or even 135° C.) for a considerable period, say 15-20 hours. A homogeneous dense product results. The resin softens at temperatures above 40° C. but never actually melts without decomposition. The insoluble product possesses high dielectric strength and good insulating properties. The resin may be molded with a filler in various ways. Alkali acts upon the resin to reconstitute glycerol and phthalic acid. Callahan also proposes to use glycol and carbohydrates, such as glucose, saccharose, starch, and cellulose in place of glycerol.

Final Product.

The resin described above does not represent the final product. Callahan found this resin to be affected by water. On standing for several weeks in contact with water the insoluble resin became white and cheesy upon its surface. Long exposure to the weather caused it to become white and crumbly. Callahan termed this product an intermediate resin and made further experiments on the effect of heat treatment leading to a final form of resin of notable resistance to water.¹¹ The procedure recommended is to heat the intermediate product for 5-10 hrs. at 180°-250° C. At this temperature condensation is completed and any traces of free glycerol are eliminated. The resin is insoluble in all the usual solvents but like the intermediate product is soluble in glycerol. The final product is not attacked in the cold by alkaline solutions. At 140° C. the resin becomes leathery and may be bent or molded.

Retardation of Conversion.

If fillers are to be impregnated with the molten resin a difficulty arises that at the temperature required, hardening takes place, rendering impregnation difficult. Callahan avoids this difficulty by adding naphthalene or anthracene to the resin. Monochlor and tetrachlor naphthalene also can be used. 13-18 per cent of naphthalene is recommended.¹²

Malic Acid.

134 parts malic acid and 92 parts glycerol are heated to 110° C. Ebullition occurs and the temperature is raised gradually to 235° C., yielding a flexible and somewhat sticky resin. It is soluble in acetone and is fusible at approximately 100° C. Heating for a period of about 15 hrs. at a temperature below the fusing point but rising to 100° C. yields an infusible resin.¹³

Camphoric Acid. $C_8H_{10}(COOH)_2$.

46 parts of glycerol and 100 parts of camphoric acid are heated to 100° C. when the mixture becomes uniform in appearance. The temperature is increased slowly to 250° C., yielding a resin soluble in acetone, slightly soluble in methyl and ethyl alcohol and insoluble in benzol. The resin is clear and yellow in color, melting at 110-130° C. It may be hardened by heating for some time at 90-135° C.¹⁴

¹¹ U. S. Pat. 1,108,330, Aug. 25, 1914.

¹² U. S. Pat. 1,108,331, Aug. 25, 1914.

¹³ Callahan, U. S. Pat. 1,091,627, Mar. 31, 1914.

¹⁴ U. S. Pat. 1,091,628, Mar. 31, 1914.

Mixed Acid Resins.

Thus far the resins described have been obtained mainly by reaction with only one acid. The next advance in these polyhydric resins was made when it was found that mixtures of acids gave less brittle products. The combination with glycerol of both an aromatic acid (phthalic) and an aliphatic acid (oleic, butyric, succinic, citric, etc.) as mentioned above imparts a toughness to the resin not found in the single acid product. Arsem¹⁵ obtains a double ester by reacting with an amount of one acid insufficient to combine with all the alcoholic hydroxyl, then completing the esterification by means of a different acid. In illustration, 184 parts by weight of glycerol and 296 parts of phthalic anhydride are heated to 200-210° C. until gas evolution ceases. 118 parts of succinic acid are added and the mixture is heated to 210-225° C. until the consistency becomes jelly-like. Upon cooling a brittle, hard, transparent resin, free from bubbles, is obtained. This product, according to Arsem, appears to be the glycerol ester of phthalic and succinic acids, and has a cyclic structure. It is not fusible but becomes plastic on heating and may be molded with fillers and the molded product hardened by heating ½ hour at 200-210° C. Callahan¹⁶ prepares a fusible resin by heating 118.4 parts by weight of phthalic anhydride (4/5 mol.), 141.5 parts succinic acid (1 1/5 mol.) and 184 parts glycerol (2 mols.). This material is converted into an infusible, insoluble product by heating for a protracted period at 85-150° C. At 85° C., 15 hours heating is needed; at 150°, 10 hours is sufficient. The time of heating varies not only with the temperature but also with the composition. Arsem states that tartaric, glutaric, camphoric and malic acids may be used instead of phthalic acid and that glycol and mannitol also may be used in lieu of glycerol. Various mono or di basic acids may be employed to finish the esterification, e.g., propionic, stearic, palmitic, oleic, benzoic, lactic, salicylic, glycollic, chloracetic, chlorbenzoic and chlorpropionic acids. Glyceryl phthalate treated with stearic acid forms a soft substance resembling paraffin. When glyceryl phthalate is heated with ordinary rosin, which contains an acid anhydride, a hard reddish-brown resin is obtained. By the same treatment, lactic acid gives a resin of great plasticity. The flow point is 64° C. One molecular proportion each of glycerol, phthalic anhydride and monochloracetic acid affords a soft, sticky resin melting at 64.5° C. Reduction in the proportion of chloracetic acid yields a resin of flow point 88°, becoming infusible on heating 8 hours at 160° C.

Oleic Acid.

One molecular proportion of glycerol combines with about 1½ mols. of phthalic acid. Arsem¹⁷ obtains a mixed acid resin by replacing

¹⁵ U. S. Pat. 1,098,776, June 2, 1914.

¹⁶ U. S. Pat. 1,108,332, Aug. 25, 1914.

¹⁷ U. S. Pat. 1,098,777, June 2, 1914.

1/6 of the phthalic acid by an equivalent amount of oleic acid. Thus 92 parts by weight of glycerol are heated with 148 parts phthalic anhydride to 200-210° C. until evolution of gas decreases; 141 parts of oleic acid and 37 parts of phthalic acid are now added. At first two layers are formed but after heating to 200-215° C. reaction occurs and a deep red liquid is obtained which requires further heating to 220-230° C. The product congeals at room temperature and is soluble in benzol and turpentine. By heating to 160° C. for 20-30 hours an insoluble, infusible but flexible product is obtained. When this phthalic-oleic resin is heated with sulphur a very rubbery mass results.¹⁸

Butyric Acid.

A somewhat similar procedure employing butyric acid as the secondary or auxiliary acid is that of Friedburg.¹⁹ 2 parts by weight of phthalic anhydride and 1 part of glycerol are heated gradually to 185°, then to 210° C. giving a fusible, soluble resin. 22 parts of this resin are dissolved in glycerol and 10 parts butyric acid are added. Heating is conducted under a reflux condenser for 8-24 hours. Then the product is heated in an open vessel to 300° C. until distillation ceases. A soft rubber-like brownish mass, soluble in acetone, results.

Improving Flexibility.

The addition of certain substances to promote flexibility of the citric acid resin has been proposed by Dawson,²⁰ meta dinitrobenzene, ethyl benzoate, acetanilide and beta naphthol being serviceable. A mixture is made from 11.4 parts of citric acid, 5 parts glycerol and 5 parts methyl alcohol. To this is added from 1 to 10 parts of the flexibilizing agent. Articles to be impregnated are dipped into the solution and baked at 125° C. to drive out the alcohol and start the reaction which is completed at 150-200° C.

Castor Oil.

Howell²¹ and Dawson^{21a} find castor oil improves the toughness and flexibility of the various glycerol resins described above. Howell reacts on 184 parts of glycerol with 296 parts of phthalic acid. The temperature is quickly raised to 130° C., then gradually increased to 180° C. 320 parts of castor oil are added and the temperature finally is carried to 220° C. If carried to 280° C. a violent evolution of gas occurs and an infusible vesiculated product results. 18 hours heating at 150° C. will render the material infusible without the formation

¹⁸ Arsem, U. S. Pat. 1,082,106, Dec. 23, 1913.

¹⁹ U. S. Pat. 1,119,592, Dec. 1, 1914.

²⁰ U. S. Pat. 1,085,112, Jan. 27, 1914.

²¹ U. S. Pat. 1,098,728, June 2, 1914.

^{21a} U. S. Pat. 1,141,944, June 8, 1915.

of bubbles. Dawson employs the glyceryl esters of phthalic, cinnamic, citric and succinic acids. In one instance he prepares a resin from glycerol, phthalic and oleic acids and castor oil. He also proposes the employment of castor oil with other mixed esters, for example, from phthalic acid with lactic, palmitic, benzoic or salicylic acids. One formula is: glycerol 92 parts, phthalic anhydride 148 parts, heat to 200° C., then add oleic acid and castor oil 70.5 parts each and phthalic anhydride 37 parts. The reaction is exothermic and the temperature may rise spontaneously to 260-270° C. but should be held, by cooling if required, at about 200° C. to complete the reaction.

Shellac.

Weisberg²² finds that the incorporation of shellac with glycerol polybasic acid resins affords a mixture of good molding properties. The water resistance of the fusible synthetic resin is improved by the presence of shellac. As shellac is not noted for its water-resisting qualities, the benefit to be derived in this respect hardly can be considered substantial.

Polyglycerol Resin.

An inspection of the preceding pages of this chapter will show the effort which has been expended on the development of organic acid resins particularly from the standpoint of the properties induced by specific acids. The base—glycerol—has been taken for granted. Weisberg and Potter have departed from the beaten track and have given attention to glycerol itself. The result of their investigations is polyglycerol resin. Polyhydric alcohols are generally capable of being condensed with themselves to yield complex bodies retaining an alcoholic character. When glycerol is distilled the residue in the still contains di- and tri-glycerol, the mixture being termed "polyglycerols." They are formed by the elimination of water between two or more molecules of glycerol. By heating glycerol for a half hour at 280° C. in the presence of $\frac{1}{2}$ per cent of sodium hydroxide or acetate the greater part of the glycerol is converted into the condensation product. This condensed glycerol reacts more rapidly with organic acids than normal glycerol and its use facilitates resinification. The initial fusible or class A resin is formed in about one-fifth the time required with glycerol. The physical properties of the polyglycerol resins do not differ greatly from those made from normal glycerol. Phthalic acid or anhydride is the preferred primary acid basis but may be substituted by diphenic acid, 1, 8 naphthalic acid, benzoyl-benzoic acid, chlor benzoyl-benzoic acid and methyl benzoyl-benzoic acid. The primary acid basis, for best results, demands the presence of a secondary acid—an aliphatic acid—as a toughening agent. The polybasic acids recom-

²² U. S. Pat. 1,413,145, Apr. 18, 1922.

mended as auxiliaries are succinic, tartaric, citric, maleic, fumaric, malic and malo-malic acids.²³

Phenol Alcohols and Phthalic Anhydride.

DeLaire²⁴ has condensed a phenol alcohol with phthalic anhydride or phthalic acid, forming a transparent resin soluble in alcohol. The procedure is to dissolve in alcohol 8 parts of phenol alcohol and 2 parts of phthalic anhydride. The alcohol is removed by distillation and the residue heated on an oil bath at about 100° C. If the heat is arrested at the moment when the evolution of water appears to be ended a transparent alcohol-soluble resin results but by prolonging the action of heat a resin is obtained which is insoluble in alcohol. Coralex²⁵ states that purified phenol-aldehyde resins combine with polyvalent alcohols such as glycerol. See Chapter 8.

²³ U. S. Pat. 1,424,137, July 25, 1922. The formation of polyglycerols is discussed by Lewis, J. Chem. Soc. 1922, 122, i, 419, and by Rayner, J. S. C. I. 1922, 41, 224T.

²⁴ Belgium Pat. 192,590, 1906.

²⁵ British Pat. 148,264, 1919.

Chapter 18.

Polymerization of Vinyl Compounds. Effect of Substitution in the Ethylene Group.

Ethylene is a relatively stable body but substituted ethylenes containing a negative group or the phenyl group polymerize on standing at room temperature. Exposure to sunlight or the rays of ultraviolet light greatly quicken the rate of polymerization.

The group $\text{CH}_2:\text{CH}-$ is called *vinyl*. Vinyl chloride, $\text{CH}_2:\text{CHCl}$, and bromide, $\text{CH}_2:\text{CHBr}$, polymerize readily on standing and rapidly under the influence of light. The same change occurs in some vinyl derivatives; styrene, $\text{C}_6\text{H}_5\text{CH}:\text{CH}_2$, being an example. The unsymmetrical compounds $\text{CH}_2:\text{CHCl}$, CH_2CHBr , $\text{CH}_2:\text{CCl}_2$, $\text{CH}_2:\text{CBr}_2$, $\text{CH}_2:\text{CClBr}$ polymerize quite easily.¹ These substances are readily oxidized by air or oxygen. Trichlorethylene, $\text{CHCl}:\text{CCl}_2$, on the other hand, is not spontaneously polymerized and is not readily oxidized when kept in contact with oxygen. The same relative stability appears also in the compounds allyl chloride, $\text{CH}_2:\text{CH}.\text{CH}_2\text{Cl}$, and the bromide, also in symmetrical dibromethylene, $\text{CHBr}:\text{CHBr}$.

Vinyl chloride, $\text{CH}_2:\text{CHCl}$, exposed to sunlight forms a polymeric amorphous insoluble body of specific gravity 1.406 which melts above 130°C . with decomposition.² Difluorethylene, $\text{CH}_2:\text{CF}_2$, does not oxidize in the air nor polymerize in sunlight. Fluorobromethylene, $\text{CH}_2:\text{CFBr}$, on the contrary, oxidizes easily and polymerizes to a solid body. Vinyl bromide, $\text{CH}_2:\text{CHBr}$, polymerizes quickly in sunlight and slowly in diffused light.³ A trace of iodine hinders the polymerization in diffused light according to Kutscherow.⁴ The polymerized form is an amorphous solid of specific gravity 2.075. It is not soluble in water, alcohol nor ether. At $125\text{--}130^\circ\text{C}$. the polymer begins to decompose. Boiling alcoholic potash does not eliminate bromine. Chlorbromethylene, $\text{CH}_2:\text{CClBr}$, quickly changes to a solid, amorphous polymer. Biltz⁵ allowed polymerization to progress for 8 days. The polymer $(\text{C}_2\text{H}_2\text{ClBr})_x$ was insoluble in all common solvents. It was somewhat soluble in boiling nitrobenzol and in molten naphthalene.

¹ Ber. 1879, 12, 2076; Brooks, "Non-Benzenoid Hydrocarbons," New York, 1922, 211.

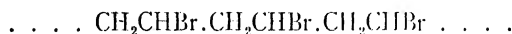
² Baumann, Annalen, 163, 317; Beilstein, 4th Ed., 1, 186.

³ Bauman, Annalen 163, 312; Beilstein, 4th Ed., 1, 189; Lwow, Ber. 1878, 11, 1258.

⁴ Ber. 1881, 14, 1533.

⁵ Ber. 1902, 35, 3527.

On standing in sunlight, vinyl bromide, $\text{CH}_2\text{:CHBr}$, according to Ostromislenski, is converted into the compound α -caouprene bromide. The presence of other substances and various external conditions affect the extent of polymerization. Thus, light volatile hydrocarbons greatly retard the change. α -Caouprene bromide is quite resistant to energetic oxidizing agents and to concentrated mineral acids. Exposure to ultraviolet light causes polymerization to progress further forming what are termed β - and γ -caouprene bromides. The beta compound is soluble in carbon bisulphide. The gamma compound swells in this solvent but does not dissolve. Ostromislenski⁶ regards the structural arrangement of the polymers of vinyl bromide to be as follows:



Dibromethylene, $\text{CH}_2\text{:CBr}_2$, is a liquid easily changing into a solid polymer which is insoluble in water, alcohol and ether.

Polymerization is a property which is probably common to all substances possessing an ethylene linkage, but great variations in polymerization tendencies appear, based on structural differences and substituents. The adaptation of polymerization changes to industrial purposes has been urged as a means of obtaining, from vinyl compounds, amorphous bodies or resins capable of use in making various plastic products. Clear and colorless masses, relatively resistant to flame or non-inflammable, are obtained which can be molded and machined.

The products obtained⁷ by the polymerization of vinyl halides, with or without the addition of other substances, are softened or dissolved by means of suitable solvents, and subsequently reconverted into the solid form.⁸ These products are non-inflammable and odorless, and according to Chem. Fabrik Griesheim-Elektron may be used in substitution for cellulose esters or celluloid.⁹

Vinyl esters, particularly the acetate or chloracetate, are perhaps better suited for the purpose than the halide compounds. Polymerization may be effected by heating alone. If this be carried out in a mold, a shaped article is obtained. Vinyl acetate and chloracetate are readily polymerized by actinic rays.¹⁰

As noted above, the unsymmetrical ethylene compounds, which polymerize, are rather easily oxidized. Polymerization is accelerated by oxidizing agents. Those best adapted to assist the polymerizing effect are organic peroxides or ozonides and organic acid anhydrides in conjunction with percarbonates, perborates, silver oxide or other

⁶ J. Russ. Phys.-Chem. Soc. 1912, 41, 204.

⁷ Chem. Fabrik Griesheim-Elektron; German Pat. 281,877, July 4, 1913.

⁸ J. S. C. I. 1915, 623.

⁹ See French Pat. 474,086, 1914; J. S. C. I. 1915, 724.

¹⁰ Chem. Fabrik Griesheim-Elektron, J. S. C. I. 34, 623 and 724; German Pat. 281,687, July 4, 1913; Kunststoffe 1921, 10.

metallic oxides capable of yielding oxygen.¹¹ Benzoyl peroxide has been recommended as a catalyst. For example, 0.5-1 gram of benzoyl peroxide is mixed with 1 kilogram of vinyl chloroacetate, and the mixture is heated carefully in a large vessel provided with a reflux condenser. At 80-100° C. the polymerization begins with a rapid rise in temperature, so that the reaction vessel must be cooled. If the contents are diluted with an indifferent solvent, such as chlorobenzene (300 grams), the violent progress of the reaction is moderated. The product is a thick syrup which can be worked further in various ways, e.g., by illumination of the syrup, the solid products desired are obtained in a short time, inasmuch as the unaltered vinyl ester polymerizes. These solid masses can also be obtained by driving off the vinyl ester and the diluent *in vacuo*.¹² Modifying agents such as camphor may be added to the esters before polymerization. Coloring materials also may be introduced.

The various products obtained are proposed for making buttons, horn substitutes, combs, umbrella handles, plates, films or threads.

Varnishes or lacquers may be prepared by dissolving the polymer in an appropriate solvent. Ethyl acetate may be used as a solvent for polymerized vinyl acetate to form a dipping lacquer. As in the manufacture of pyroxylin lacquers, a cheaper solvent vehicle may be produced by a mixture of a good solvent with a low-priced non-solvent such as benzine, benzol and chlorbenzol.¹³ The following active solvents are specified:

Ketone Solvents: acetone, methyl ethyl ketone and acetophenone; *nitrohydrocarbons:* nitromethane and nitrobenzene; *aldehydes:* benzaldehyde and salicylaldehyde. Solutions of the polymer prepared with these solvents may be thinned with benzol or other cheap diluent. For example, 20 parts by weight of polymerized vinyl acetate are dissolved in a mixture of 10 parts acetone, 15 parts of cyclohexanone and 5 parts of benzol.¹⁴

Plotnikow¹⁵ observes that solutions of vinyl chloride in 99 per cent ethyl alcohol, acetone, carbon tetrachloride, methyl alcohol, ether, and toluene when exposed to the action of ultraviolet light at temperatures between 15.2° and 25.2° C. deposit a pure white powder as polymerization product. In the presence of salts of manganese, cobalt, nickel, copper, vanadium, and uranium, the reaction is catalysed and takes place in visible light. The process is carried out to advantage in the

¹¹ German Pat. 281,688, July 4, 1913; Klatte and Rollett, U. S. Pat. 1,241,738; J. S. C. I. 1917, 1185; Chem. Abs. 1918, 231.

¹² British Pat. 15,271, June 25, 1914.

¹³ Chem. Fabrik Griesheim-Elektron J. S. C. I. 1916, 698; German Pat. 291,299, May 8, 1915; Addition to 290,544; Chem. Abs. 1917, 11, 1913; Cf. Chem. Abs. 1915, 9, 149 and 356.

¹⁴ Other solvents mentioned are trichlorethane, methylene chloride, cyclohexanol ester, also the ethylidene esters of acetic, lactic and salicylic acids. Acetone and epichlorhydrin are recommended for cementing articles made of the vinyl ester polymer.

¹⁵ Z. wiss. Phot., 1922, 21, 117; J. S. C. I. 1922, 41, 261A.

presence of uranyl salts in sunlight. The product resembles rice powder and is slightly soluble in acetone, methyl alcohol, and ethyl alcohol, more soluble in benzol, chlorbenzol, carbon tetrachloride, and carbon bisulphide and very soluble in phenyl acetate. From those solvents in which it is fairly soluble the polymer may be obtained as an elastic film which loses its elasticity on keeping. On mixing with 40 per cent of cedar oil, 40 per cent of French turpentine, 65 per cent of pine oil, or 60 per cent of camphor, yellow waxes are produced; 30 per cent of castor oil converts it into a somewhat sticky whitish-gray mass, and with 60 per cent of copaiba balsam it yields a dark wax-like mass; with 70-75 per cent of castor oil or 75 per cent of pine oil it yields a vaseline-like mass. Jellies are produced on mixing with 50-72 per cent of aniline or 70-85 per cent of tetralin (tetrahydronaphthalene) while with 40 per cent of tetralin, 50 per cent of Peru balsam, or 23 per cent of rosemary oil it gives a solid elastic mass.

The application, industrially, of this interesting type of reaction has been hindered by the absence of methods of making vinyl compounds cheaply. The utilization of acetylene as a raw material is a promising direction of endeavor. The following method by Plauson¹⁶ has been proposed for making vinyl compounds and their polymerization products. The addition of hydrogen halides, methyl halides, or organic carboxylic acids to acetylene hydrocarbons takes place smoothly and rapidly at 100-120° under a pressure of 1 to 2 atmospheres. By increasing the pressure and by raising the temperature when all the acetylene is absorbed, polymerization products of the vinyl esters are obtained without the necessity of isolating the intermediate product. The reaction can be accelerated by the addition of small amounts of certain metals or metallic compounds such as magnesium, tin, or copper, or their compounds, iodine, hydriodic acid, boron compounds, or organic acid anhydrides. If the acetylene is diluted with an inert gas such as nitrogen, or with benzol or petroleum vapor, the pressure can be increased to 10-15 atmospheres or more and the reaction correspondingly accelerated without risk of explosion of the acetylene. Examples: (1) 40 parts of allylene and 36-38 parts of dry hydrogen chloride are heated at 120° C. at 1 to 2 atmospheres' pressure for 10 to 24 hours. Yields of 80-85 per cent of β -chloropropylene and 10-15 per cent of another chloro compound result, and the former can be completely polymerized by further heating at 150-200° C. The polymerization is accelerated by increasing the pressure to, say, 15 atmospheres by the introduction of nitrogen. The polymerization product can be employed for the preparation of varnishes. (2) 26-28 parts of acetylene are gradually introduced into a mixture of 50 parts of acetic acid and 1 part of acetic anhydride. The mixture is heated at 40-60° C. and the pressure raised to 5 atmospheres by the introduction of nitrogen. The product consists of 75 parts of vinyl acetate and 3.5 parts of ethylidene diacetate. If the temperature is then increased to 120-

¹⁶ Traun's Forschungslaboratorium G.m.b.H., J. Chem. Soc. 122, i, 516; British Pat. 156,117, 1920; U. S. Pat. 1,425,130, Aug. 8, 1922.

200° C. and the pressure to 10 atmospheres or more, the esters are polymerized to products which vary in consistency from semi-liquids to more or less tough solids, according to the extent to which the polymerization is allowed to proceed.

Vinyl halides¹⁷ also are obtained by the action of concentrated aqueous hydrogen halides at 60-95° C. on calcium carbide in the presence of a catalyst, a mixture of a mercury and a copper salt being suitable. The reaction occurs without catalysts if the pressure is increased above atmospheric, but some of the vinyl halide is polymerized under these conditions. The vinyl chloride distills off as it is formed, and if a stream of hydrogen chloride is passed through the reaction mixture during the operation the yield is almost quantitative. Small quantities of zinc, aluminum, or tin chlorides accelerate the addition of hydrogen chloride to form vinyl chloride, but ferric chloride accelerates the reaction in the direction of the formation of dichloroacetaldehyde, which is normally present in small amount as a by-product.

Vinyl sulphuric acid and its homologues are prepared by forcing an acetylene hydrocarbon under pressure into concentrated sulphuric acid cooled to a temperature below 0° C., preferably in the presence of a catalyst such as mercuric sulphate. Alkyl ethers of vinyl alcohol and its homologues result from the interaction of an alcohol with these acid sulphates.¹⁸

Ethers and esters of ethyleneglycol and vinyl alcohol are produced by passing acetylene together with the vapor of compounds containing hydroxyl or carboxyl groups over heated catalysts, especially metals, their oxides and salts. Examples of suitable catalysts are cadmium, zinc, mercury, magnesium, barium, copper, silver, cerium, nickel and iron, or their compounds, preferably mounted on a support such as charcoal, pumice or infusorial earth. The reaction may be carried out under increased or reduced pressure; and is preferably conducted as a cyclic process, the unchanged hydroxyl or carboxyl compound being continuously separated from the product and returned with fresh acetylene into the reaction chamber. According to an example, equal volumes of acetylene and acetic acid are passed at a temperature of 200° C. over charcoal impregnated with cadmium acetate; ethylidene diacetate is isolated from the condensed product.¹⁹

Vinyl Compounds, Phenol and Formaldehyde.

Vinyl compounds, such as esters, ethers, or halides, or their condensation products, are heated with phenol and formaldehyde, or hexamethylenetetramine, or with phenol-formaldehyde condensation products, for the production of artificial resins. Accelerators, such as organic anhydrides or peroxides, or non-explosive ozonides, may also be added. Condensation may be effected in the presence of low-boiling solvents, e.g., methyl alcohol, ethyl alcohol, or acetone, and the solution may then be used for impregnating wood or the like, the

¹⁷ British Pat. 156,120, 1920, J. Chem. Soc. 121 and 122, i, 517.

¹⁸ British Pat. 156,121, Dec. 30, 1920; Chem. Abs. 1921, 1728. Influence of potassium hydroxide on the formation of vinyl alcohol from acetaldehyde, see Evans and Looker, J. Am. Chem. Soc. 1921, 43, 1925. Note also Plauson, U. S. Pat. 1,436,288, Nov. 21, 1922.

¹⁹ Consortium für Elektrochemische Industrie Ges., Chem. Met. Eng. 1922, 27, 706.

presence of uranyl salts in sunlight. The product resembles rice powder and is slightly soluble in acetone, methyl alcohol, and ethyl alcohol, more soluble in benzol, chlorbenzol, carbon tetrachloride, and carbon bisulphide and very soluble in phenyl acetate. From those solvents in which it is fairly soluble the polymer may be obtained as an elastic film which loses its elasticity on keeping. On mixing with 40 per cent of cedar oil, 40 per cent of French turpentine, 65 per cent of pine oil, or 60 per cent of camphor, yellow waxes are produced; 30 per cent of castor oil converts it into a somewhat sticky whitish-gray mass, and with 60 per cent of copaiba balsam it yields a dark wax-like mass; with 70-75 per cent of castor oil or 75 per cent of pine oil it yields a vaseline-like mass. Jellies are produced on mixing with 50-72 per cent of aniline or 70-85 per cent of tetralin (tetrahydronaphthalene) while with 40 per cent of tetralin, 50 per cent of Peru balsam, or 23 per cent of rosemary oil it gives a solid elastic mass.

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¹⁶ Traun's Forschungslaboratorium G.m.b.H., J. Chem. Soc. 122, i, 516; British Pat. 156,117, 1920; U. S. Pat. 1,425,130, Aug. 8, 1922.

potassium ferrocyanide; little or no resin is formed and vanillin is recovered in 95 per cent yield.

Allyl Malonate.

A balsam may be prepared from allyl malonate by simply heating for 24 hrs. at 170° C. in a closed enamelled vessel.²⁹

Allyl Cinnamate.

A more drastic heat treatment yields hard resins. Allyl cinnamate is heated for 36 hrs. at 170° C. in a similar closed vessel, after which the temperature is held at 230° C. for another 36 hrs. The cinnamate is converted to an amber-colored resin.

Styrene or Phenyl Ethylene.

This substance, also called styrol, polymerizes on heating with the formation of an insoluble substance metastyrene, $(C_8H_8)_x$. When styrene was studied by Simon in 1839 the solidification of this substance was observed and was attributed to oxidation. Blyth and Hofmann³⁰ observed styrene to change to metastyrene, or metastyrol on heating at water bath temperature for 3 days or by rapidly heating in a sealed tube for one-half hour at 200° C. Exposure at room temperature to sunlight brought about polymerization in three weeks. Miller³¹ obtained the meta compound by heating styrene with sodium bisulphite solution to 100-120° C. Concentrated sulphuric acid also brings about the polymerization.³² Metastyrene is an odorless, transparent substance of vitreous lustre. It is insoluble in water and alcohol and only slightly soluble in boiling ether. Most reagents have very little action although Blyth and Hofmann found that by boiling with concentrated nitric acid a nitrometastyrene resulted. The production of styrene cheaply no doubt would bring it into immediate use in the field of plastics.

Kronstein³³ discovered the polymerization of styrene progressed in two stages. He heated the styrene in a closed vessel and observed thickening to occur without loss of solubility in benzol. A stage was reached at which gelatinization suddenly occurred and the product was no longer soluble in benzol. When the heating was continued the gelatinous material was converted into a glassy solid. Kronstein therefore considers the polymerization of styrene to occur in two stages, (1). The phase involving thickening and ending with the instant of gelatinization. (2.) The phase beginning with gelatinization yielding products insoluble in benzol.

A sample withdrawn during the first stage or phase, dissolved in benzol and precipitated with alcohol yielded a thick oil which gradually became thicker and at length could be drawn into threads. Eventu-

²⁹ Kronstein, U. S. Pat. 843,401, Feb. 5, 1907.

³⁰ Ann. 53, 291 and 311.

³¹ Ann. 189, 361.

³² Berthelot, Bull. soc. chim. 6, 296.

³³ Ber. 1903, 35, 4154, note also *ibid.* 4150.

ally the product became solid. It could be easily pulverized and melted below 100°C . When placed in boiling water it melts and after a time becomes filled with bubbles and then solidifies. The further investigations of Kronstein showed that gelatinization occurred when about one-half of the styrene was converted into the intermediate product represented by the first phase of polymerization. When equal weights of the intermediate product and styrene were heated the former dissolved in the styrene and the solution became converted into a coagulum. Metastyrene subjected to distillation yielded about 60 per cent of styrene and the residue was soluble in benzol. This indicates reversion or depolymerization of the metastyrene to the intermediate stage.

Phenyl Vinyl Ketone.

Acetophenone and formaldehyde in the presence of ammonium chloride give trimethylol acetophenone. When distilled with steam an oil is obtained, which, on standing for a few days, becomes a horny mass of noteworthy hardness. This substance is considered by van Marle and Tollens¹⁴ to be polymerized phenyl vinyl ketone.

Linseed Oil Substitute.

Melamid,¹⁵ who has made many proposals in the field of synthetic resins, prepares a substitute for linseed oil by reacting at 100°C . with allyl or vinyl bromide on solutions in 20 per cent caustic soda of the hydroxy alcohols made from meta or para cresol and formaldehyde. The product is diluted with water and the solution is extracted with ether or acetone. After distillation of the solvent a viscous light brown liquid is obtained which rapidly dries in the air.

¹⁴ Ber. 1903, 36, 1351.

¹⁵ German Pat. 352,003, 1920; J. S. C. I. 1922, 41, 728A.

Chapter 19.

Sulphur Resins.

While the main portion of the present chapter is devoted to organic resins containing sulphur in combined form the utility of elementary sulphur in this field should not be overlooked. Chemically, of course, sulphur cannot be classed with the resins; but its hardness, vitreous fracture and melting point give it certain features common to resins. In fact, if roll sulphur or brimstone were dyed a red or brown color, it would resemble various common resins in general appearance so closely that from a superficial examination the sample might easily be pronounced a resin.

Because of its tendency to crystallize sulphur has very little prospective value in liquid coating compositions. That is, a solution of sulphur when applied with a brush to a surface and allowed to dry forms a crystalline coating of no particular value. When added to the organic substances used in varnishes it may completely change their nature. For example, Chinese wood oil, which is a rapid drying oil, loses its drying qualities when only a small percentage of sulphur is chemically combined with it.

As a preliminary to the discussion of sulphur-containing resins, the author wishes to digress further to consider the properties of sulphur as a binding agent, a subject seemingly remote from that of synthetic resins.

Elementary sulphur as a binding agent has certain fields of application which appear to be promising. Its cheapness as compared with any other fusible binding agent makes possible its use in various channels where higher priced binders would be prohibited. Also sulphur has a marked resistance to acids, oxidation and weathering influences.¹ It is fairly hard and its melting point is sufficiently high for many purposes. It has fairly good insulating qualities. The disadvantages of sulphur are its brittleness and tendency to crystallize. Also under some conditions a surface of sulphur may become very slightly oxidized so that the material develops an acid reaction, causing metals to rust.

The author has made various molded articles from mixtures of sulphur and a filler by hot pressing and although these articles do not have a degree of strength nor a surface finish which is equal to many

¹The employment of sulphur in conjunction with phenol condensation products to impregnate tubes of paper pulp as carried out by Burningham, Richter, Van Arsdel and White, U. S. Pat. 1,396,201, Nov. 8, 1921, is illustrative of the adaptability of sulphur for waterproofing purposes.

of the resin-containing products one striking feature is that the sulphur molded articles have little or no action on the steel molds. Prior to the investigation made by the author the criticism had been advanced that sulphur would blacken the molds. Although no exhaustive tests were made in this direction the preliminary pressings which were made did not indicate the sulphur to have any immediate action.

Bacon and Davis² have made tests on mixtures of sulphur and sand used for casting acid-resisting pipe and recommend 40 parts by weight of sulphur to 60 parts of sand. The latter should not contain any constituent which will be attacked by any substance with which it is to come in contact in the finished form. Thus in the case of acid tanks the sand employed should be free from limestone or other constituents affected by acids. The sulphur is melted in a kettle with constant stirring and the sand is separately heated, then poured into the sulphur while the stirring is continued. If the sand is not heated it will chill the sulphur and form lumps. Crushed coke is a better filler than sand. The addition of one per cent each of naphthalene and heavy mineral oil to sulphur decreases its brittleness.³

A much more interesting application of sulphur is its possibilities in the plastic form as a binding agent in molded goods. As is well known sulphur when strongly heated changes to an allotropic form which is rubbery and elastic. It retains this plastic condition, however, only a few hours after heating to the plasticizing temperature. The author has made a sufficient number of experiments on the problem of retaining sulphur in a plastic condition to believe that it will be possible to make use of sulphur commercially in this form. Although molten sulphur combines with many resins and other organic substances these products in turn are not readily soluble in molten sulphur. The sulphur resins, however, made by treating phenol with sulphur chloride which are discussed later in this chapter do have the property of dissolving in molten sulphur and when put into solution in this manner have a pronounced retarding effect on the conversion of plastic sulphur to the crystalline form. Some method of this character may in due course of time afford the means of utilizing so cheap a material as sulphur in molded goods where a certain degree of elasticity is required, and in which sulphur plays the part of the essential binding agent.

² Met. Chem. Eng. 1921, 24, 70.

³ Bacon and Davis believe that sulphur should find a much wider range of usefulness on account of its being one of our cheapest raw materials. The properties of sulphur which suggest a wider range of application are its very poor conductivity of heat and electricity, its resistance to being wetted by water and its inertness towards most acids, all combined with a fair degree of physical strength. These properties suggest heat-insulating materials, electrical insulators of various types, water- and acid-proof cements and acid-proof construction material. The properties of sulphur which are not desirable are its brittleness and inflammability. The brittleness can be reduced or overcome sufficiently for many purposes by incorporating with sand, asbestos or paper pulp or by reinforcing with a wire screen. In many cases the inflammability is not a serious objection. Met. & Chem. Eng. 1921, 24, 70.

Olefine Sulphur Dioxide Resins.

The reaction between lower olefines and sulphur dioxide producing glassy clear white solids is a peculiar and interesting case of resinification. Matthews and Elder⁴ find that reaction does not take place in the dark but occurs readily in sunlight or ultraviolet light. Thus pseudobutylene, $\text{CH}_3\cdot\text{CH}:\text{CH}\cdot\text{CH}_3$, yields the complex $(\text{C}_4\text{H}_8\text{SO}_2)_n$. Reaction is effected by mixing the liquid butylene with an excess of liquid sulphur dioxide and exposing, in a sealed glass tube, to sunlight for several days. The liquids are perfectly miscible and the progress of the reaction may be followed by the separation of oily drops, which sink. The oily layer increases with the length of the illumination period and towards the end of the reaction some of the complex may separate in a solid state. When the reaction is complete the tube sometimes contains only a viscid substance impregnated with sulphur dioxide. At other times the viscid material is admixed with a white substance. On opening the tube the sulphur dioxide escapes, leaving a spongy substance. When all dioxide and butylene, if any, have been eliminated, a horny or glass-like clear solid remains. Equal weights of propylene and sulphur dioxide condensed, by means of a freezing mixture, in a glass tube and exposed to sunlight after sealing the tube yield a white, friable mass. Amylene and sulphur dioxide in equal molecular proportions are caused to combine by illumination or by warming in a water bath to about 50° C.

Ethylene.

Sulphur dioxide reacts far more slowly with ethylene than with the preceding hydrocarbons. Ethylene is passed into liquid sulphur dioxide, cooled to -80° C. until the dioxide is well charged. The mixture is exposed to light for a protracted period.

The butylene product is soluble in chloroform and acetylene tetrachloride and is softened but not dissolved by acetone. It possesses the advantage of not being readily inflammable and Matthews and Elder propose the substitution of the butylene complex for celluloid and some of the resins. Mixed with celluloid it reduces the inflammability of the latter.

Propylene and Sulphur Chloride.

The reaction between sulphur monochloride and propylene or butylene is strongly exothermic and at 110° C. a black resinous product is very readily formed with evolution of hydrogen chloride.⁵ Dried propylene was passed into sulphur monochloride (40 grams) at a rate of about a litre per hour, the absorption vessels being kept at constant temperature. At 60° C. the sulphur monochloride soon became brown and gelatinous, and finally changed into a viscid, black product

⁴J. S. C. I. 1915, 670; British Pat. 11,635, 1914.

⁵Pope and Smith, J. Chem. Soc. 1921, 119, 397.

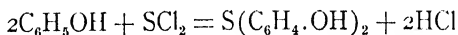
through which the gas would not pass. During the whole time much hydrogen chloride was evolved. When distilled in a current of steam the product furnished only about 1 gram of volatile oil.⁶

Sulphur Chloride—Phenol Resins.

The chlorides of sulphur, both mono- and di-chlorides, react violently with phenol, cresol and immediate homologues forming resinous bodies having a notably high sulphur content. In view of the ease with which these resins are prepared and their low cost of manufacture together with the possession of certain qualities peculiar to these bodies on account of their content of sulphur, adaptation in due course to industrial uses may be expected. The first to prepare resins from sulphur chloride and phenol was Tassinari⁷ who observed the formation of resins when phenols were treated with the dichloride of sulphur.

Tassinari's Resin.

The observation was made by Tassinari in 1887 that mixing sulphur dichloride and dry phenol caused a violent reaction. To moderate the reaction, Tassinari diluted both the dichloride and the phenol with carbon disulphide, cooled and added the dichloride solution in small portions to the phenol solution. At every addition the mixture became black and liberated hydrochloric acid, becoming decolorized again in a short time. After having remained for some hours in the refrigerating bath, a solid yellow substance floated on top of the clear, somewhat yellowish liquid. Removal of carbon disulphide by distillation left a yellow, half-solid mass rich in sulphur. The solid material was dissolved in caustic potash solution and on dilution with five times the volume of water much resin separated. This was of a soft viscid consistency and greenish yellow in color. The resin was removed and carbon dioxide passed through the aqueous solution. Another resin first precipitated and then crystalline scales. The crystalline material proved to be the compound hydroxyphenyl sulphide, $S(C_6H_4.OH)_2$. The reaction leading to its formation is as follows:⁸



Tassinari considered the resin to be produced by a secondary reaction, presumably from the monochloride which is formed from the dichloride during the inevitable heating of the reaction mixture. By treating the resin with nascent hydrogen it is converted largely into hydroxyphenyl sulphide (dioxathiobenzene) and this conversion led Tassinari to conclude the resin to be hydroxyphenyl disulphide (dioxidithiobenzene). Resins also were formed on treating parabromphenol, tri-

⁶ Coffey, J. Chem. Soc. 1921, 94.

⁷ Gaz. chim. Ital. 1887, 17, 83 and 90.

⁸ In this equation no account is taken of the resin which is always formed in greater or smaller amounts depending on the temperature conditions.

chlorphenol, nitro phenols, ortho and para cresol and thymol with sulphur dichloride. With beta naphthol the reaction proceeded slowly but a violent reaction took place on treating alpha naphthol in carbon disulphide with sulphur dichloride, even when the reaction mixture was cooled to a low temperature. After distilling the solvent a yellow resinous mass remained from which Tassinari was unable to obtain any product of definite chemical composition.⁹

Alcohol-Soluble Cresol Sulphur Chloride Resin.

The following method has been used in the author's laboratory for making an alcohol-soluble sulphur resin from cresol. A good quality of commercial "metaparcresol" is mixed with an equal volume of toluol and while stirring an amount of sulphur monochloride one and one-half times the weight of the cresol is slowly added. The operation should take place under a hood or in apparatus provided with means for absorbing hydrogen chloride as the evolution of this acid is copious. The reaction is accompanied by marked evolution of heat and the solution of resin in toluol, while still hot, may be distilled to eliminate toluol and simultaneously deodorize the resin.

Deodorization.

The resin contains traces of chlorphenols or other bodies having an odor somewhat resembling iodoform and to remove this "chemical smell" the resin is deodorized by blowing with steam or air in enamelled or lead-lined receptacles. In the procedure under consideration the solution was blown with air at about 150° C. (302° F.) to 170° C. (338° F.). Blowing for ¼ to ½ hour suffices to remove toluol and the impurity causing the odor. The solvent may, of course, be recovered.

Acidification.

When the hydrochloric acid is completely expelled from the resin the color of the latter changes from light yellow to a brown. To restore the color a very small amount of phosphoric acid may be added. This may be added to the resin most conveniently after solution in alcohol. A few drops of a 20 per cent solution of phosphoric acid in acetone suffice to turn the brown solution to a light yellow color. Too large a quantity of phosphoric acid must be avoided as it may cause precipitation of the resin from alcoholic solution. Phosphoric acid also may be added to the molten resin after air blowing. Due to moisture present in the cresol or other causes, some free sulphur is formed and enters into solution in the alcoholic menstruum. On standing for some time the sulphur separates and deposits as a yellow

* * Sulphur dyes have been prepared from a basis derived by reacting on 1 part of phenol with 2 parts of sulphur monochloride. Poirrier, U. S. Pat. 646,873, April 3, 1900; 740,465, Oct. 6, 1903. See also German Pat. 103,646 relating to the treatment of amido phenol with 3 parts by weight of sulphur chloride.

precipitate. It sometimes contains a variable amount of cresol resin of high sulphur content which normally would be insoluble in alcohol, but which is carried into solution initially and subsequently slowly separates. For this reason aging of such solutions is desirable. The alcohol solution made to a strength of five pounds of resin to the gallon may be used as a substitute for shellac in many applications. The cresol resin dries hard enough to be readily sandpapered and has a satisfactory lustre.

Fusibility.

A wide range of softening points is obtainable with resins made from phenol or cresol and sulphur chloride; a range which depends upon the proportion of sulphur chloride employed. Phenol (C_6H_5OH) requires a considerably higher proportion of sulphur chloride than cresol to obtain a resin having the same softening point. For example, a resin prepared by treating 100 parts by weight of "metaparcresol" with 150 parts of sulphur chloride produces a hard, non-tacky resin, softening at about $115^\circ C$. To obtain a resin having the same softening point from phenol it is necessary to employ 250 parts of sulphur chloride to 100 parts of phenol. The latter proportion with cresol would yield a nearly infusible resin whereas to obtain with phenol a product similarly heat-resistant about 350 parts of sulphur chloride should be used. Resins prepared from 100 parts phenol and various proportions of sulphur monochloride have the following properties, the appearance being observed at room temperature.

Parts of Sulphur Chloride.

- | | |
|-----|--|
| 75 | Light yellow, sticky, liquid about the viscosity of glycerol. Soluble in alcohol, benzol, acetone, sulphur, phenol and many other organic solvents. |
| 125 | Darker yellow, sticky, liquid about the viscosity of molasses. Soluble in alcohol, benzol, acetone, sulphur, phenol and many other organic solvents. |
| 175 | Dark yellow, tacky solid, slightly plastic. Readily soluble in alcohol-benzol or alcohol-acetone mixture, phenol and other solvents. |
| 225 | Dark yellow, hard resin, softening at about $100^\circ C$. |
| 250 | Dark yellow, hard resin, softening at $115^\circ C$. The 225 and 250 proportion are soluble in the same solvents as 175 but solubility decreases with increased content of sulphur. |
| 300 | Dark yellow, hard resin, softening at high temperatures. Partially soluble in mixtures of highly volatile solvents. Soluble in phenol, aniline, and other high boiling solvents. |
| 350 | Dark yellow, hard, tough, almost infusible resins, insoluble in common volatile solvents. Soluble in phenol and aniline. |

All these resinous products are soluble in aqueous solutions of caustic alkalies. They dissolve quite readily in molten sulphur.

Sulphur Resin, Phenol and Formaldehyde.

McCoy¹⁰ utilizes Tassinari's resin in conjunction with phenol-formaldehyde condensation products. He treats phenol with any of the chlorides of sulphur (monochloride, S_2Cl_2 , preferred) and moderates the reaction in some cases, as did Tassinari, by the use of a solvent. Carbon tetrachloride is employed by McCoy while Tassinari used carbon disulphide. The resin is dissolved in phenol and the mixture treated with formaldehyde. No proportions are given by McCoy. Another mode is to solidify a fatty oil and phenol in any proportion by sulphur chloride. The solidified product is dissolved in an additional quantity of phenol and heated with formaldehyde or its polymers to bring about further reaction.

Factis.

Fatty oils which have been treated with sulphur chloride to make "oil rubber" or "factis" are considered by McCoy¹¹ to be a desirable addition to phenol-formaldehyde condensation products. 120 parts of factis are dissolved in 300 parts of phenol by heating. 320 parts of 40 per cent aqueous formaldehyde are added and the mixture is heated to 100-125° C. to eliminate water. Further heating causes the resin to thicken and harden, finally becoming insoluble and infusible. Plasticizing substances, viz., camphor or glycerol, may be added. Asbestos, mica, silica, wood flour and other fillers may be incorporated, also rubber and nitrocellulose.¹²

Sulphochloride Resins.

Resin-like substances are obtained by treating aromatic sulphochlorides with salts of resinic, humic, or lignoceric acids,¹³ e.g., to a solution of 120 kg. of sodium colophionate in 100-200 kg. of water is added 100 kg. of α - or β -naphthalene sulphochloride with stirring, the solution being heated to 30° C. for 12 hours. The liquid is allowed to cool, and the solid product separated by decantation or filtration, and dissolved for the purpose of purification in an organic solvent, e.g., benzol, which is then evaporated. Or the organic acid salts are replaced by soft coal-tar pitch, anthracene oil distillates obtained in the production of hard pitch therefrom, or the alkali-soluble phenolic portion of soft pitch or anthracene oil, in the presence of alkali, e.g., 100 kg. of soft pitch containing 20 per cent of alkali-soluble matter, are heated with sufficient caustic soda lye to neutralize the acidity, allowed to cool while stirring constantly, and about 24 kg. of ortho- or para-toluenesulphochloride in benzol added. After stirring for 12 hours, the benzol solution is separated from the aqueous layer, washed with water until neutral, dried over calcium chloride, and the solvent distilled off in vacuo.

¹⁰ U. S. Pat. 1,194,201, August 8, 1916; British Pat. 13,657, June 12, 1913; French Pat. 458,904, June 6, 1913; J. S. C. I. 1913, 1163.

• ¹¹ U. S. Pat. 1,194,201, Aug. 8, 1916.

¹² For a discussion of Nuth's process of treating factis with amines see Chapter 23.

¹³ Melamid, British Pats. 133,712 and 133,713, Oct. 11, 1919.

Sulphur Chloride Plastic.

Reif¹⁴ sprays finely divided fibrous fillers (peat, wood, cork, paper) with oils, tars, fats or a mixture of these materials with resins and when the particles of filler are well coated, the mass is treated with sulphur chloride. The latter converts the sticky coating into a more or less hard and elastic substance. To neutralize the acid, the filler is first treated with gaseous ammonia or dusted with hydrated lime or carbonate of soda. The composition can be worked on heated rolls, tube machines and presses to form articles of a varied character. The composition hardens during the molding or shaping operation. Mineral fillers, coloring agents and fireproofing salts may be added.

Yellow or orange-colored petroleum jellies or waxes obtained as residual products in the distillation of crude petroleum, yield black bitumen-like products when they are treated in the fused state with 1 to 5 per cent or more of sulphur chloride, the proportion of the latter being varied according to the degree of hardness it is desired to give to the product. The sulphur chloride may be dissolved in 10 to 20 per cent of its weight of carbon disulphide, coal-tar naphtha, etc. Heat is applied to the mixture until the evolution of gas has ceased. The fused mass is then run into molds. The melting point of the product is 20 to 40° C. higher than the initial material. Chlorine and sulphur dissolved in carbon disulphide act less rapidly than sulphur chloride.¹⁵

Aniline and Sulphur Chloride.

The reaction between aniline and sulphur chloride is very violent and a neutral solvent should be used to mitigate the reaction. Schmidt¹⁶ obtained from aniline and sulphur chloride diluted twenty fold with benzol, a small amount of mono-thio-aniline together with resinous products. These he attributed to the formation of dithioaniline. Coffey¹⁷ observed the formation of dithioaniline, $C_6H_5NS_2$ (dithiophenylamine), as a thick reddish oil on treating an excess of aniline at -10° C. with sulphur chloride well diluted with ether. The dithio compound increased in molecular weight on standing, indicating polymerization. The N:S union is not a very stable one. The author has prepared resins from aniline and toluidine, employing proportions of sulphur monochloride ranging from below 1 part by weight to about 1½ parts. The higher proportions of the chloride give very brittle insoluble products. The lower proportions give less brittle substances but in no case have any resins of particular interest from a commercial standpoint been obtained. Benzol serves as a satisfactory diluent and the product should be well washed to remove aniline hydrochloride.¹⁸

¹⁴ U. S. Pat. 895,197, Aug. 4, 1908; note also J. S. C. I. 1921, 427 A; German Pat. 332,941, Jan. 3, 1920.

¹⁵ LeRoy, Bull. Soc. Ind. Mulhouse 1907, 77, 147; J. S. C. I. 1907, 598 and 754; Chem. Abs. 1907, 2409.

¹⁶ Ber. 1876, 9, 1050 and 1878, 11, 1168.

¹⁷ Rec. trav. chim. 1921, 40, 747.

¹⁸ Many investigations on the interaction of various amines and sulphur chloride have been carried out. See Claus and Krall, Ber. 1871, 4, 99; Smith

Phenol and Sulphur.

Artificial resins are produced by heating an oxy compound of an aromatic hydrocarbon with sulphur in the presence of a basic substance in proportion not greater than one-fifth of that necessary for neutralizing the oxy compound.¹⁰ The product may be rendered infusible and insoluble by the action of heat, or heat and pressure. These resins may be produced more cheaply than those of the phenol-formaldehyde type. The sulphur may be used in the proportion of 2 to 3 equivalents to one of phenol or cresol, and about half of this sulphur is evolved as hydrogen sulphide. Further quantities of sulphur and alkali sulphide may be taken up as a filling material. The reaction may be accelerated by the addition of a catalyst such as a halogen or a compound yielding a halogen. If a small proportion of formaldehyde is added, a harder resin is obtained. One method of preparation is to fuse a mixture of phenol 47 parts and sulphur 32 parts in apparatus equipped with a reflux condenser, and add 1 part of potassium hydrogen sulphide and heat the mixture to 130-140° C. The reaction continues with increasing temperature and terminates when the evolution of hydrogen sulphide ceases. A viscous fluid resin is obtained which becomes solid on cooling, and is soluble in alcohol, acetone, benzol, and alkalies, but insoluble in acids, aliphatic hydrocarbons, and halogen derivatives. The resin becomes infusible and insoluble on prolonged heating to 150-180° C. The resin also may be obtained from (1) ortho-cresol, sulphur and potassium carbonate, (2) phenol, tricresol, sulphur and aniline, with a small proportion of iodine, (3) resorcinol, sulphur and sodium hydroxide, (4) α -naphthol or β -naphthol, sulphur and sodium hydroxide, (5) as in the first illustration with a small proportion of hexamethylene-tetramine which may be in aqueous solution.

Krafft and Lyons,²⁰ on heating phenyl sulphide with sulphur for 30 hours, found that sulphur was taken up and on further heating they obtained a resinous product.²¹

A resinous or tarry product is obtained by heating lactic acid with sulphur chloride. 1 part of the latter reagent may be used to 2 parts of lactic acid.

Vulcanized Glycerol Phthalate.

A vulcanized glycerol resin obtained by Arsem²² has qualities somewhat resembling rubber. 92 parts by weight glycerol and 148 parts of phthalic anhy-

1875, 8, 1445; Hannimann, Ber. 10, 403; 12, 681; Holzmann, Ber. 21, 2063, note also 1636 and 19, 1570; Kym, Ber. 21, 2807; 23, 2458; Michaelis, Ber. 1895, 28, 165. Amido compounds and sulphur chloride, Naik, J. Chem. Soc. Trans. 1921, 119, 1166. From salicylamide Naik obtained an amorphous solid which melted and decomposed at 226° C. Dithio-ketones and dithio-ethers, Naik, *ibid.* 379 and 1231.

¹⁰ Soc. of Chem. Ind. in Basle; Chemical Age, London, 1922, 7, 610; British Pat. (application) 186,107, June 9, 1921; Blumfeldt, U. S. Pat. 1,435,801, Nov. 14, 1922.

²⁰ Ber. 1896, 436.

²¹ For data on resinification by heating of thioureas (thiocarbamides) see Chapter 13.

²² U. S. Pat. 1,082,106, Dec. 23, 1913.

dride are heated to 200-210° C. until gas bubbles cease rising. 282 parts of oleic acid are added. Continued heating at 210-215° C. causes the resin and oleic acid to mix. Heating at 230° C. for several hours is required to complete the reaction. 20 parts of sulphur are now added and heating continued until a dark brown elastic mass is formed.²⁰

Alkali-Resistant Resin.

Formaldehyde reacts with ammonium sulphhydrate to yield a resinous body²¹ and Diesser²⁰ has sought to make technical application of the resin because of its noteworthy resistance to alkalis. Protracted boiling with alcoholic potash has little or no effect on the resin. The condensation product is dissolved in chloroform, tetra or pentachlorethane and articles coated or impregnated with the solution. Fillers and coloring agents may be added to the solution.²⁰

Ammonium Thiocyanate and Formaldehyde.

Ammonium thiocyanate combines with formaldehyde in concentrated aqueous solution in equimolecular proportions without production of carbon dioxide. The condensation product can combine with further quantities of formaldehyde forming bodies which, however, are less stable and readily part with some formaldehyde. The products are amorphous yellow compounds without definite melting points and are practically insoluble except in strong acids and strong alkalis, which decompose them into their components.²²

Experiments conducted in the author's laboratory with ammonium thiocyanate and formaldehyde indicated a harder resin could be obtained by using formaldehyde in excess of equimolecular proportions. Ammonium thiocyanate was dissolved in the minimum amount of water required to put it into solution and admixed with aqueous 40 per cent formaldehyde solution, using equimolecular proportions. The mixture was heated to about 50° C. and the yellow solution became turbid and a yellow resin precipitated. Water was poured off and the product was dried at 110° C. for several hours. When hot it was a yellow viscous liquid which solidified on cooling to an opaque light yellow mass. It was brittle and possessed a disagreeable odor. The resin was insoluble in alcohol, benzol, acetone, and mixtures of these, either hot or cold. It was also insoluble in water. In aniline and phenol the resin dissolved and could be precipitated by adding alcohol or benzol. When two molecular proportions of formaldehyde were used the reaction progressed spontaneously after being started by gently heating. The conversion proceeded with rising temperature and a hard amorphous precipitate formed and settled. This was collected and dried. It was found to be soluble in cresol on gently heating although there were some signs of decomposition. The odor of both of these resins when heated is very disagreeable.

Thiobenzaldehyde, obtained by prolonged treatment of benzaldehyde with hydrogen sulphide, first sinters between 80-90° C. then melts. A polymer of

²⁰ For further particulars relative to the preparation of polyhydric ester resins see Chapter 17.

²¹ *Ann. chim. phys.* 1898, 7, Series 15, 3, 571.

²² German Pat. 246,038, Dec. 17, 1910.

²³ Cf. Thiofurfural, Chapter 11.

²⁴ Schmerda. *Z. angew. Chem.* 1917, 30, 176; *J. S. C. I.* 1917, 36, 942.

thioanisaldehyde exhibits amorphous tendencies. Protracted treatment of an alcoholic solution of methyl salicyl aldehyde with hydrogen sulphide yielded a viscous reddish mass.²⁸

Toron.

The product which is sold at the present time under the trade name of "toron" was discovered by Pratt²⁹ while working on a solvent for reclaimed rubber in which turpentine was the base. During his experimental work sulphur was introduced into the material and on heating it was observed that the sulphur and turpentine formed a black viscous material. The composition varied in viscosity and hardness, depending on the time and temperature of the operation. A hard product similar to mineral rubbers was obtained on long heating at elevated temperatures. The product was found to be readily soluble in benzol, toluol, xylol, gasoline and other hydrocarbon solvents and partially soluble in acetone and alcohol. Recent studies on the chemical constitution of this sulphur-terpene compound indicate the composition $C_{20}H_{26}S_7$, or perhaps some multiple of this formula.

Solutions of toron have penetrating qualities which render them useful for impregnating cotton fibre, paper or other tissues. In its commercial form toron has a density of 1.24 and a viscosity similar to that of molasses at room temperature. Approximately 4 per cent of the compound can be distilled with steam and an equal amount will distil at a temperature of approximately 165-170° C. On prolonged heating at elevated temperatures decomposition proceeds with the evolution of considerable quantities of hydrogen sulphide. In carrying out the manufacture on a commercial scale equal parts of sulphur and turpentine are heated gradually to 165° C. in a kettle fitted with a reflux condenser. Care should be taken to have the application of heat very gradual because hydrogen sulphide is evolved and the reaction may become uncontrollable if heat is too strongly applied. The reaction should be completed at the expiration of 16 hours.

The most important application for toron is in the impregnation of cotton fabric employed in the manufacture of tires and rubberized belting. The fabric is immersed in a solution of toron in a hydrocarbon solvent. The latter is subsequently removed by drying and during this operation great care is taken to avoid fires. The drying is carried out in a current of an oxygen-free gas circulating through the drying chamber and an absorption device which removes the solvent. By keeping air away from the material during drying the danger incident on handling inflammable solvents in this manner is reduced to a minimum. The fabric is then frictioned and skimmed on a rubber calender as is customary in all rubber factories using untreated fabric. A slight change in the composition of the rubber compound is recommended in order to allow for the accelerating effect

²⁸ Baumann and Fromm, *Ber.* 24, 1436; 1444 and 1446.

²⁹ U. S. Pat. 1,349,999, Aug. 17, 1920; British Pats. 165,662; 169,031; 169,514; 169,777, 1920; *Chem. Abs.* 1922, 502, 802 and 850. *J. Ind. Eng. Chem.* 1923, 15, 178.

of toron on the rate of vulcanization. The impregnated fabric besides being proof against mildew and decay affords a better bonding effect with the rubber.⁸⁰

Sulphuretted Copal.

Zingler⁸¹ takes about 50 kilograms of powdered gum copal and from 7½ to 15 kilograms of flowers of sulphur. These are heated under continual agitation with double the quantity of turpentine to a temperature of 125-150° C. till completely dissolved. Ammoniacal solutions of casein and tannic acid are added and the plastic mass is washed with cold water.

Sulphuretted Rosin.

By adding sulphur to molten rosin Valenta⁸² obtained a clear mass which on heating turned brown, frothed up and gave off hydrogen sulphide; at 250° C. this evolution of gas is regular until it ceases, when the mass becomes brownish-black. The product contains sulphur, is pitchy, and closely resembles Syrian asphalt in properties. It is insoluble in alcohol, but dissolves readily in chloroform and benzol; a thin layer of the latter solution, when allowed to dry on glass, deposits a solid varnish which is sensitive to light.

Sulphur as a Resin Hardener.

According to Prager⁸³ rosin may be hardened by the addition of 5-10 per cent of sulphur at 140-150° C. The cooled product is dark green in color, possesses a sulphur-like odor, and is quite resistant to the action of the weather or chemical reagents.

When rosin, Manila copal, dammar and similar resins are heated under pressure with an aqueous suspension of sulphur a hardening effect and an improved resistance to oxidation results, according to Low.⁸⁴

Sulphurized Oil and Lime.

Linseed, cotton and castor oils or other drying or semi-drying oils react with zinc oxide or hydrated lime, when heated to 200° C., to a product which is hard but porous and disintegrated by water. Barringer⁸⁵ finds the addition of sulphur to yield an impervious mass, not attacked by water. One composition is (parts by weight) zinc oxide 20, sulphur 8, ground flint 40, powdered talc 12, asbestos 20, and linseed oil 15 to 20. After thorough mixing the composition is molded and the molded articles baked at a temperature ranging from 150° to 220° C. for from 4 to 8 hours. The reactions of saponification and vulcanization are best carried out at 200-220° C. A product made within these temperatures may be soaked in water for weeks without apparent deterioration. Although articles made by Barringer's process have a slightly grayish tone instead of the bluish black color preferred by molders, the method has been applied commercially in a successful manner over a number of years.

⁸⁰ The author wishes to acknowledge the courtesy of Mr. Theodore S. Sullivan, Jr., of the Clapp Products Company, Boston, Mass., in furnishing information concerning toron.

⁸¹ J. S. C. I. 1883, 287; German Pat. 20,939, Apr. 15, 1882.

⁸² Centr. Org. f. Waarenkunde u Tech. 1891, 1, 19; Chem. Z. Rep. 1891, 12, 211.

⁸³ Seifen-Z. 1915, 706.

⁸⁴ U. S. Pat. 1,243,312, Oct. 16, 1917.

⁸⁵ U. S. Pats. 1,085,102, Jan. 27, 1914, and 1,111,430, Sept. 22, 1914.

Artificial Asphalts.

Numerous suggestions are to be found for making artificial asphalts and bitumen-like substances by the treatment of oils, fats, tars, etc., with sulphur or sulphur chloride. Thus, anthracene residues treated with sulphur yield a product of high tenacity which may be used in lacquers.³⁶ Or a mixture of fish oil, oleic acid and sulphur is heated and the product used in varnishes.³⁷ Again, oils are treated with sulphur chloride and the purified material added to balloon varnish.³⁸ Asphaltum and rubber in solution are treated with sulphur or the monochloride and made the basis of an antifouling paint.³⁹ Titzel⁴⁰ makes a baking japan or varnish containing gilsonite and sulphur. A discussion of the many sulphured compounds or compositions of this general character is beyond the scope of the present volume.⁴¹

³⁶ Verkaufsvereinigung f. Teererzeugnisse G.m.b.H., German Pat. 332,888, Aug. 12, 1919; J. S. C. I. 1921, 427A.

³⁷ Plauson and Vielle, British Pat. 156,144, 1920.

³⁸ Ballonhullen-Ges. m.b.H., German Pat. 321,264, Jan. 25, 1918; Chem. Abs. 1921, 15, 1083.

³⁹ Ivinston and Roberts, British Pat. 161,201, July 12, 1919; J. S. C. I. 1921, 399A.

⁴⁰ U. S. Pat. 391,927, Oct. 30, 1888.

⁴¹ See also Chapter 5.



Chapter 20.

Nitro Resins.

Although nitro resins are of frequent occurrence in the course of nitration of organic bodies not many of these have been described and very few appear to have promising commercial applications. This is due in some cases to the bad odor or to the unstable character of the products. Some of these even when gently heated decompose rather violently. In other cases the strong red color characteristic of many of the nitro resins is an objection. Red resins of this character are not infrequently observed by investigators in the explosive field. For example, in one of the processes of making picric acid a resin of this character is produced.

Asphaltic Distillates.

One of the few attempts at practical application of nitro resins has been made by Forrest and Meigs.¹ They destructively distil asphalt or asphaltic petroleum or materials such as gilsonite, thereby obtaining a distillate containing a large proportion of unsaturated bodies. A fraction of the distillate boiling between 204° and 316° C. (400-600° F.) is selected from which to obtain a resin of medium hardness. This distillate is placed in a jacketed vessel through which steam or water may be passed. Nitric acid (of strength 43° B.) is added very slowly. The reaction is a very violent one accompanied by the evolution of heat and the addition of acid should be made very cautiously. Forrest and Meigs recommend that the volume of acid dropped at any one time on the oil should not exceed the ratio of 1 to 2500. The oil is heated to about 93° C. (200° F.) and the temperature should not be allowed to rise above 104° C. (220° F.). When 100 parts by volume of acid have been added to 200 parts by weight of the oil the reaction is stopped. The product is a light yellow semi-solid resin. The reaction mixture is cooled when the resinous matter separates, or the reaction mixture may be poured into cold water and the resinous product separated in this way. It is soluble in methyl and ethyl alcohols and acetone but insoluble in petroleum ether and carbon bisulphide.

Fractions of higher boiling point yield hard resins. A very viscous oil with properties which Forrest and Meigs find to closely resemble those of nitrated castor oil may be obtained by using a distillate from

¹U. S. Pat. 1,305,790, June 3, 1919.

gilsonite boiling up to 204° C. (400° F.). These nitro resins are recommended as additions to pyroxylin compounds as, for example, in the preparation of lacquers, leather dressings and artificial leather. In the use of the resin for the latter purpose it may be mentioned that the odor of these nitrated hydrocarbons in the crude state would probably preclude their use in artificial leather. The manufacturers of pyroxylin artificial leather employ castor oil as a softening agent and the odor of the castor oil after it has been exposed in the leather substitute for some time is objectionable. On unrolling a sheet of artificial leather containing such rancid castor oil the odor is quickly apparent. As the crude nitro hydrocarbon resins appear scarcely to represent any improvement over castor oil with respect to odor it is not likely that they can be used without deodorization, which by the way is probably a difficult matter. The attention of investigators in this field of synthetic plastics is called to the need for a softening agent capable of mixing with nitrocellulose in all proportions and not giving any unpleasant odor to the leather substitute nor increasing its inflammability. A considerable amount of study has already been given by manufacturers of nitrocellulose products to this problem.

In the writer's laboratory a dark brown or black resin has been obtained by passing oxides of nitrogen into a highly unsaturated light distillate obtained in the manufacture of Blau gas.

Petroleum Oils.

The preparation of a nitro-resin is carried out by Edeleanu and Filiti² as follows: petroleum oil or petroleum distillate is run slowly into a well-stirred mixture of strong nitric and sulphuric acids, so long as a brown color (but not a black color) remains. The temperature is kept below 80° C. Three parts of mixed acid are used with one part of petroleum distillate, specific gravity .890. The acid consists of five parts by weight of sulphuric acid to one part of nitric acid. The sulphuric acid can be concentrated or anhydrous. Unchanged oil is skimmed off. The acid solution of the nitro-product is diluted with water which causes the nitro-product to precipitate and sink while some oily material rises to the surface. The precipitated nitro-product is washed with water and dried. In another modification the mixed acid may be added to the oil until a brown color is formed and the unchanged oil separated. The product is fairly soluble in alcohol, more soluble in acetone. It can be added to other resins for the production of plastic materials or varnishes.

Asphaltum.

Day³ slowly adds powdered asphaltum, e.g., gilsonite, grahamite, albertite, to nitric acid (strength not specified but apparently concentrated), while continuously stirring. The temperature should

¹U. S. Pat. 745,802, Dec. 1, 1903.

²U. S. Pat. 967,337, Aug. 16, 1910.

not go too high, but apparently can be raised nearly to the boiling point of the acid. The undissolved matter is then skimmed off and discarded. The solution contains nitro products, and is poured into a large amount of water, which precipitates the nitro bodies. Most of these sink to the bottom. The part which floats is skimmed off and discarded. The heavy precipitate is then washed with water until free from nitric acid and is dried. This product may be dissolved in alcohol, ether, benzol, or naphtha to form a varnish.

Nitrated Rosin.

Resins prepared by the nitration of rosin or oil of turpentine have been used by Fry⁴ in the preparation of varnishes. As the resulting nitro compound is subsequently decomposed by heating, the ultimate resin is probably more accurately described as an oxidation product. In fact, Fry terms the resins "oxycolophones" and "oxyturpentines." Fry's process is included in the present chapter, however, as his procedure is primarily one of nitration. Thus powdered rosin is kneaded with nitric acid, 1.42 sp. gr. adding the acid drop by drop and avoiding the formation of lumps. A dark olive green powder containing nitrocolophony results. This material is introduced in small successive quantities into a porcelain basin over a boiling water bath. The nitrated material fuses, becomes brown, then begins to froth. A yellow resin is obtained which may be used in making oil varnishes.⁵

The nitration of Venice turpentine or a mixture of 2 parts rosin to one part of oil of turpentine is carried out by adding nitric acid very gradually while cooling the reaction mixture. To 100 parts of the material to be nitrated 10 parts of nitric acid may be used for soft, 30 to 35 parts acid for hard products. Rosin is more easily nitrated than Venice turpentine and the latter more quickly than oil of turpentine. Consequently when rosin is dissolved in oil of turpentine the result varies according to the length of time allowed for nitration. To restrict the action chiefly to the rosin, the acid is allowed to act only one or two hours, the reaction then being brought to an end by heating on the water bath. Oil of turpentine requires a period of several days to form a resin satisfactorily.

Care should be taken both in the nitration and the decomposing (oxidation) steps to avoid working with large portions at one time. Much heat is generated and the nitro compound is in fact a mild explosive. *Accelerated reaction due to the heat developed in the treatment of large batches may result disastrously unless due precautions are taken.* The resins obtained may be deepened in color by heating for several hours above 212° F. but below 400° F. (204° C.). Resins of an orange or red tint are obtained which can be used in varnishes required to produce a staining effect.

⁴U. S. Pat. 754,298, Mar. 8, 1904.

⁵The proportions recommended by Fry are 100 parts by weight of rosin to 10 to 30 parts by volume of nitric acid.

Resins made by the use of lower percentages of nitric acid are readily soluble in boiled oil and oil of turpentine. Those prepared with higher proportions of acid are less soluble, due, according to Fry, to dehydration during the heating stage. Oil varnishes made from "dehydrated oxyturpentine," if found too thick can not be thinned successfully by heating and adding oil of turpentine. A better way is to mix a batch which is too thick with one that is too thin. Good blending is obtained in this manner.

The rosin may be nitrated in the presence of drying oil. Thus 100 parts rosin are heated with and dissolved in 50 parts of the drying oil. 10 to 15 parts of nitric acid are added carefully. The batch is decomposed on a water bath or sand bath. When decomposition takes place there is a pronounced swelling of the mass, greater than that occurring when oil of turpentine is the raw material. The resins obtained from turpentine or rosin according to the above procedures are soluble in alcohol, and spirit varnishes may be made from such resinous products.

Other Nitrated Substances.

A nitro product obtained by Flexer⁶ on treating petroleum tar mixtures with nitric acid is used in paints and for molding purposes. Dinitrostilbene compounds on exposure to ultra violet light are extensively resinified.⁷ Nitrated castor oil has been used in admixture with nitrocellulose under the name of "Velvrit." Unlike untreated castor oil, the nitrated material mixes in all proportions with nitro cotton. Solutions of the mixture may be used as varnishes.⁸ Reif⁹ nitrates oil, tar, fat or a mixture of these materials with resins, the nitration being conducted in the presence of a filler. The composition may be molded.

Nitrophenylhydrazine.

By the interaction of p-nitrobenzenediazonium chloride and sodium sulphite a comparatively stable p-nitrophenyl-hydrazine-disulphonate is formed. To obtain a good yield of p-nitrophenylhydrazine the sulphite solution must be maintained neutral or alkaline throughout the addition of the diazo solution, otherwise, or when sodium bisulphite is used, the diazo-sulphonate separates as an unstable orange mass which redissolves to react with more sodium sulphite with difficulty, and readily decomposes with formation of a resin.¹⁰

⁶ *Kunststoffe* 1921, 12; Austrian Pat. 74,127

⁷ Stoermer and Oehlert, *Ber.* 55B, 1232.

⁸ *J. S. C. I.* 1899, 975.

⁹ *U. S. Pat.* 895,197, Aug. 4, 1908.

¹⁰ Davies, *Chem. Soc. Trans.*, 1922, 121, 715; *J. S. C. I.* 1922, 41, 435A.

Chapter 21.

Halogenated Rubber. Chlorinated Rubber Solutions.¹

A number of substances are obtained by treating unvulcanized rubber with halogens, the reaction usually being accomplished in solution. While strictly speaking these products probably should not be termed resins as their properties are more or less intermediate between those of rubber and true resins, nevertheless the substances have more resemblance both in properties and use to resins than to rubber and consequently are included here. Chlor rubber is characterized by a light color and toughness which varies with the degree of halogenation; and a solubility which is greater than that of rubber and likewise varies with the amount of halogen introduced. The various chlorinated rubbers are all considerably more brittle than rubber, but, with the exception of some of the highly chlorinated grades, are very flexible when compared to most resins, some of them being comparable to pyroxylin in this regard.

Action of Chlorine: Early Work.

It has been known for some time that the various halogens would react upon rubber and yet very little appears to have been done in the way of commercial application of the products. Among the early work on record is that of Alfred V. Newton² in 1859 who described the action of gaseous chlorine on solid rubber and gutta-percha. The gum swells to a brittle white mass and the excess chlorine is then washed out with water. The product is soluble in carbon disulphide, chloroform, benzol and naphtha. The action upon dry rubber, however, is rather slow and is facilitated by first dissolving the rubber in a solvent such as chloroform or benzol. This solution, which is dark originally becomes yellow as chlorine is passed in and the reaction proceeds. The product is then flexible and limp. Continued passage of the chlorine yields a harder product. This is also soluble in the usual solvents for rubber and is precipitated by alcohol.

Gladstone and Hibbert³ did considerable work on the reactions of the halogens on rubber. This was done principally from the stand-

¹ Mr. Norris Boehmer, connected with author's laboratory, kindly assisted in the preparation of this chapter.

² British Pat. 2734, Dec. 2, 1859.

³ J. Chem. Soc. 1888, 53, 679.

point of analytical and structural research. When chlorine was passed into a one per cent chloroform solution of rubber in weak diffused light, fumes of hydrogen chloride began to come off immediately. The chlorinated compound was obtained in yellowish scales by evaporating the solvent. The composition of the chlor rubber obtained varied and no simple additive compound was formed, some substitution taking place simultaneously with the addition. The best specimen prepared contained 65.18 per cent of chlorine and corresponded approximately to the formula $C_{10}H_{14}Cl_3$.

Bromination.

The action of bromine on the rubber solution was similar to that of chlorine, fumes of hydrogen bromide being evolved immediately. Compounds corresponding approximately to the formulas $C_{10}H_{16}Br_4$ and $C_{10}H_{15}Br_6$ were obtained.

A tetrabromide of rubber similar to that obtained by Gladstone and Hibbert was likewise prepared by Weber.⁴ A chloroform solution of rubber was used in this case likewise. After the bromine had been introduced and allowed to react, the tetrabromide was precipitated by means of alcohol. This compound is stated to be insoluble in hydrocarbons, ether, acetic acid, acetic anhydride or carbon disulphide. It is unaffected by strong acids in the cold with the exception of concentrated nitric, but dissolves with partial decomposition in warm aniline, pyridine or quinoline. It is soluble in piperidine in the cold. Likewise, rubber tetrabromide is said to be soluble without heating in chloroform and thiophenol. On heating to 60° C. it begins to decompose and this decomposition becomes more rapid as the temperature is elevated. The residue is dark brown and still contains bromine.

Chemical Reactions of Rubber Tetrabromide.

Boiling alcoholic caustic soda has very slight action on the tetrabromide,⁵ but sodium ethylate is more active especially above 100° C. The action probably consists of the substitution of ethoxyl groups for bromine. A remarkable reaction occurs when the tetrabromide is added to melted phenol. At 60° C. a change of color is noticeable. The mass next becomes gummy and a brownish-purple solution begins to form, with the evolution of hydrogen bromide. From this solution an ochre-colored, easily powdered mass may be recovered which is said to be readily soluble in aqueous and alcoholic caustic soda, alcohol, acetone, ether, or ethyl acetate, but insoluble in benzol, chloroform, carbon bisulphide, or petroleum ether. Its analysis indicates that the substance is a tetroxyphenyl derivative of rubber, although a similar substance prepared at temperatures below 100° C. seemed to be a tetroxyphenol-dioxy derivative. Other similar derivatives were also

⁴ Ber. 1900, 33, 786.

⁵ Weber: "The Chemistry of India Rubber," London, 1912, 32.

prepared and all split off phenol when heated with caustic soda solutions. The cresols, carvacrol, thymol, the naphthols, resorcinol, pyrocatechol, and hydroquinone are stated to react similarly.

Pearson⁶ states that sheet rubber dipped in bromine is "vulcanized" immediately. Newbrough and Fagan used bromine and also a mixture consisting of one-third bromine and two-thirds iodine to "vulcanize" rubber. When the latter mixture was used a hard compound was obtained at 250° F. (121° C.). Rubber was chlorinated in solution by Haveman and after precipitation by means of alcohol the product was neutralized with lime or ammonia. The use of liquid chlorine is indicated by Helm who used the halogen in this form to react on a solution of rubber in benzene.⁷

Use of Iodine.

Gladstone and Hibbert state that iodine has no action on rubber in chloroform solution. Quite the contrary was observed by Weber⁸ who allowed iodine to act on a 3 per cent solution of rubber in chloroform, the proportion being 3 mols. of iodine to 1 of rubber. The solution became gelatinous in two days and absolute alcohol precipitated a straw-colored product, which was found to be entirely insoluble in all ordinary solvents. Iodine addition products of rubber have also been formed in chloroform solution, with the aid of sunlight or red phosphorus as a catalyst.⁹ It is interesting to note that while bromine and iodine derivatives, containing comparatively few atoms of the halogens, are insoluble in practically all solvents, the corresponding chlorine derivatives show a relatively great solubility, which increases with the accumulation of chlorine in the molecule.

Reaction of the Hydrogen Halides with Rubber.

Dry hydrogen chloride has also been found to react with the rubber in a manner somewhat similar to the halogens.¹⁰ Weber prepared a hydrogen chloride addition product of rubber having the formula $C_{10}H_{18}Cl_2$. This material is soluble with partial decomposition in organic bases. Hydrogen chloride splits off but some chlorine always remains with the rubber. A hydrochloride of rubber was also prepared by Harries¹¹ who used a benzol solution of the rubber. A tough mass was first obtained and by prolonged action of the hydrogen chloride a brittle material resulted. Hydrochloric acid is removed from

⁶ "Crude Rubber and Compounding Ingredients," 1909, 72.

⁷ Kirchhof, *Kolloid-Z.* 1922, 30, 176; *Chem. Abs.* 1922, 16, 1885, reports the reaction of bromine with sulphuric acid transformation products of rubber, obtaining two isomeric compounds, $C_{20}H_{30}Br_2$; also $C_{20}H_{28}Br$. Similar treatment of gutta-percha yields $C_{20}H_{32}Br$.

⁸ Weber: "The Chemistry of India Rubber," London, 1912, 36.

⁹ Hinrichsen and Kempf, *Ber.* 1913, 46, 1287.

¹⁰ Weber, *Ber.* 1900, 33, 779.

¹¹ *Ber.*, 1913, 46, 733.

the rubber hydrochloride by heating in pyridine. A chlorine-free rubber may be obtained by treating with caustic soda.¹²

Bromine and iodine compounds were made by treating the rubber with hydrobromic and hydriodic acids respectively. The reaction products have the formulas $C_{10}H_{18}Br_2$ and $C_{10}H_{18}I_2$.

Harries also caused rubber to react with hydrogen chloride using a chloroform instead of a benzol solution.¹³ The solution was saturated with hydrogen chloride and allowed to stand for 12 hours. The reaction product was then precipitated with absolute alcohol. A white elastic product was first obtained but this became more brittle upon standing. It is soluble in chloroform or benzol, but not in ether or alcohol. It has no definite melting point but begins to decompose with the evolution of hydrogen chloride at 145° , the decomposition being complete at 180° C. The formula given is $C_{10}H_{16} \cdot 2HCl$. The rate of reaction given by Harries for hydrogen chloride and rubber is much slower than that when chlorine is used. Experiments made at the author's laboratory confirm this.

Gutta-percha forms compounds similar to those of rubber with the hydrogen halides, but when these are decomposed, as by treatment with pyridine and caustic soda, the resulting product is said to resemble rubber more than gutta-percha. Gutta-percha dihydrochloride contains 34 per cent of chlorine and is grayish in color. It is tough when first prepared, but subsequently becomes brittle. At 170° it begins to give off hydrogen chloride and it breaks down completely above 200° C.

Much of the work so far described was carried out to determine the structure of the rubber molecule. Some of it was also done with the view of developing a method for the direct determination of rubber. A great deal, however, has been done toward a more practical end. The original idea was that chlorination of rubber was similar to vulcanization by means of sulphur or its compounds. Investigations show, however, that the properties of chlorinated rubber are different from those of vulcanized rubber, the chlorinated material lacking some that vulcanized rubber has and possessing other properties which the latter lacks.

Halogenation of Rubber in Solution.

Scherpe¹⁴ uses a solution in the proportion of 4 grams of Para rubber to 100 grams of carbon tetrachloride. To this is added a solution of 0.4 gram iodine in 100 grams of carbon tetrachloride. When the mixture has stood for some time it becomes less viscous and loses stickiness. The advantage claimed for the process is that it needs no heat and gives rise to no poisonous fumes. The "vulcanized" rubber is said to be useful for surgical purposes.

Heptachlorocautchouc may be produced by a process developed by S. J. Peachey.¹⁵ The rubber is first dissolved in a solvent unaffected by chlorine such as carbon tetrachloride and then treated with excess chlorine. The proportions suggested are 50 grams of plantation rubber to 1250 cc. carbon tetrachloride.

¹² See also German Pat. to Harries, 267,277, Nov. 28, 1912.

¹³ Ber. 1913, 46, 736.

¹⁴ U. S. Pat. 906,306, Dec. 8, 1908.

¹⁵ U. S. Pat. 1,234,381, July 24, 1917.

Chlorine is then passed in until 100 grams have united with the rubber, the reaction mixture being kept cool. Chlorine is partly added to the rubber molecule and partly substituted. Upon evaporation of the solvent a material somewhat resembling celluloid is obtained. A more flexible product may be produced by stopping the chlorination before it has proceeded so far.

A material resembling artificial leather may be produced by adding pigments and substances such as camphor to the chlor rubber solution and then drying out the solvent. The chlor rubber can be used in the solvent in which it is chlorinated if the acid produced in the reaction is first neutralized by means of lime or soda ash. The solution is said to be useful as a varnish or "dope" and advantages are claimed for it in waterproofing paper, fabrics, leather, etc. After applying to metals or ebonite and drying it may be baked at a moderately high temperature, giving a lustrous and strongly adherent coating. The material is also claimed to be an efficient electrical insulator.

Treatment of Scrap Rubber.

The procedures just described necessitate the use of rubber which has not undergone the usual vulcanization process. The use of scrap rubber or reclaimed rubber would materially lessen the cost of materials and a process for using these has been advocated by Bedford and Kelly.¹⁶ This process also provides for the use of new rubber and the introduction of sulphur along with the chlorine. Thus a saturated compound is obtained from the rubber which contains less halogen than if chlorine alone were used.

Starting with crepe rubber, a solution is made in a solvent unaffected by chlorine such as carbon tetrachloride. A weight of sulphur or sulphur chloride calculated according to the amount of sulphur which it is desired to introduce, is then added and chlorine is passed in until no further absorption of the gas takes place. Carbon disulphide may be used instead of sulphur chloride, the chlorine acting upon this and making the sulphur available for vulcanization.

When scrap or reclaimed rubber is used, the vulcanizing agents must first be removed by extraction with acetone or caustic alkali. The product is then suspended in a solvent and treated with chlorine, the material dissolving as it becomes chlorinated. The reaction is facilitated by plasticizing the rubber after the removal of the excess vulcanizing agent. This is done by heating the rubber to 150-170° C. (302-338° F.) with twice its weight of high boiling solvents such as pine oil, aniline and acetylene tetrachloride. The mixture is maintained at this temperature and stirred until a perfectly homogeneous solution results, which may require several hours. The solution is then cooled and an equal amount of a low boiling solvent, such as benzol, added, after which the rubber is precipitated by means of alcohol or acetone. The rubber may be redissolved and reprecipitated to eliminate the high-boiling solvent entirely. The product is soluble in any of the usual rubber solvents.

Rubber containing mineral fillers, e.g., zinc oxide, may be treated by the foregoing process, and the filler separated from the solubilized rubber by sedimentation, filtration or centrifuging.

Use of Solvents Affected by Chlorine.

A disadvantage of all these processes is the use of carbon tetrachloride or other chlorinated solvents which are comparatively expensive. The employment of a cheaper solvent, for example, benzol, would probably make a recovery operation unnecessary. The use of this vehicle

¹⁶ U. S. Pat. 1,377,152, May 3, 1921.

has been found possible by avoiding the presence of materials which might catalyze the reaction between chlorine and benzol.¹⁷ Stoneware or lead vessels may be used to carry out the reaction and the solution should be kept cool during the chlorination. Either chlorine by itself or a mixture of bromine and chlorine is employed to react on the rubber, balata or gutta-percha used. The product contains chlorine equal to twice the weight of the original rubber and is said to be suitable for use as a celluloid or leather substitute. The hydrogen chloride formed during the reaction is driven off as the solvent is evaporated or the product may be used in the original solution after neutralization with lime or gaseous ammonia.

Commercial Applications.

In recent years a chlorinated rubber material in dry form was placed on the market under the name of "Duroprene."¹⁸ Samples examined in the author's laboratory were in the form of small hard lumps mixed with finer material. In color it was slightly brownish and contained in the neighborhood of 40 per cent of combined chlorine. This form of Duroprene was soluble in benzol or its homologues, carbon tetrachloride and several other chlorinated solvents, and carbon disulphide, giving a brown solution, the depth of color depending on the concentration. Solutions more concentrated than 15 per cent were practically impossible to prepare on account of extreme viscosity. The rate of solution was not extremely rapid. The material was precipitated by alcohol, gasoline, castor oil, and like substances.

When thin layers of the solution were evaporated films were obtained which were somewhat flexible but not extremely hard. They were transparent with the exception of white spots or areas, these forming especially when comparatively concentrated solutions were used. It is reported that the solid material has been withdrawn from the market. As now marketed Duroprene is put forth in the form of varnishes and paints.¹⁹ The solvents used are principally solvent naphtha and chlorinated benzols. The solids present in these varnishes range from 8 to 10 per cent by weight. Duroprene is not offered for decorative purposes but is recommended as a protective coating for use especially in the chemical industries. It is claimed to be unaffected by acids, alkalies, turpentine, alcohol, or mineral oils.²⁰

Duroprene varnishes yield a thin, fairly hard, film which is of a light brown color, if no coloring matters have been added to the solution. Tinted varnishes are also on the market. The principal drawback in the use of Duroprene in varnishes is the fact that solutions containing much over 10 per cent become too viscous to be of use and when small

¹⁷ British Pat. 127,481, March 11, 1919, to Broadhurst, Lamble, Peachey and the United Alkali Company.

¹⁸ I. Levinstein & Co.

¹⁹ United Alkali Company.

²⁰ Chemical Age, London, 1921, 4, 508; India Rubber World, July 1, 1922; Kunststoffe, 1922, 12, 143.

proportions of solids are present, a very thin protective film results unless several coats are applied.

A film of Duroprene which has thoroughly dried is extremely resistant to penetration by hydrogen gas. Duroprene has been recom-

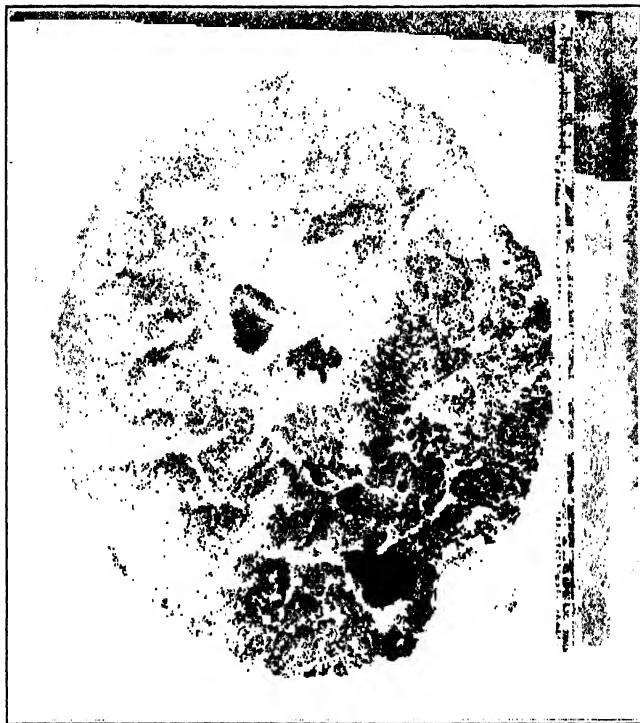


FIG. 12.—Spongy Form of Chlor Rubber.

This piece, eleven inches in diameter and about three inches thick, weighs 295 grams.

mended for use in the manufacture of insulating paper, also as a cement for porcelain and stoneware and in making rubber goods.²¹

General Properties of Chlorinated Rubber.

Several chlorinated rubbers, containing various amounts of the halogen, have been prepared in the author's laboratory. One process developed yields a solution containing 30 per cent of the chlorinated product, carbon tetrachloride being the solvent. The material obtained by the use of this process has a chlorine content in the neighborhood of 70 per cent, the dry product being obtained as a very light sponge, nearly

²¹ Gummi Z. 1922, 1266; Kunststoffe 1922, 12, 166.

white or slightly yellow in color. Another form appears as a light flaky powder. It is very readily and rapidly soluble in benzol and immediate homologues, also carbon tetrachloride, acetylene tetrachloride and carbon disulphide. Thus it is possible to handle solutions as concentrated as 30 to 40 per cent. This chlor rubber is less soluble in ethyl or amyl acetate and slightly soluble in turpentine and drying oils. The solutions are light brown in color, the shade varying with the concentration. The chlor rubber is insoluble in alcohol and gasoline.

Films made from this highly chlorinated material are more brittle, ordinarily, than those having a low degree of chlorination. Chlor rubber appears to have possibilities in impregnating paper, waterproofing cloth, etc. Used as an ingredient in varnish it lends toughness and hardness and increases resistance to water. When combined with suitable fillers it may be molded with heat and pressure. Highly chlorinated gutta-percha is more brittle than chlor rubber, and the solubility is somewhat greater.

In general the solubility of chlorinated rubber increases and the viscosity of solutions of similar concentration decreases the greater the amount of chlorine combined with the rubber up to about 70 per cent; that is, the material becomes less like rubber in its properties and more like a resin. No chlorine compound containing much over 70 per cent of the halogen has been extensively investigated. Highly brominated rubbers are practically insoluble and are hard and tough. Hardness and brittleness also increase along with the chlorine content. Material containing 70 per cent of chlorine is still very tough compared to most natural resins.

Chapter 22.

Miscellaneous Resins.

Resinous bodies have resulted in the course of reactions carried out in many researches with organic compounds. Such resins generally are not the result of an effort to produce them but are none the less interesting to investigators working in the field of synthetic resins. At the time of discovery, it may not be practicable to prepare the resin in quantity by the reaction under investigation and yet under later economic conditions this reaction may be applied to commercial advantage. This chapter will, therefore, consider miscellaneous reactions by which resinous bodies are produced but with which an insufficient volume of work has been done to warrant separate treatment. Among the resinous substances discussed are chlorinated hydrocarbons and their condensation products; certain nitrogen compounds; the benzylaniline resin of Herzog; chemical curiosities exemplified by phosphorus- and chromium-containing resins; naphthalene and a variety of its condensation products; turpentine and other hydrocarbon condensations with formaldehyde; and various other resins embracing many at present only of scientific interest in addition to those of technical promise. The chapter represents so wide a range of resinifying reactions that little attempt has been made at classification. The reader will find this chapter as heterogeneous as are the resins themselves.

Lactic Acid and Aldehyde.

Zimmermann¹ heats lactic acid *in vacuo* for a long time, raising the temperature gradually from 100° to 200° C., and condensing the product with formaldehyde or paraldehyde. An odorless, non-inflammable resinous product, soluble in chloroform and glacial acetic acid, slightly soluble in benzol, insoluble in ether, alcohol, and petroleum spirit, is thus obtained. Its color varies from pale yellow to almost black, according to the purity of the lactic acid used.

Chlorination of Cresols.

Cresol, chlorcresol, or higher homologues, when treated with chlorine at temperatures above 100° C. until nearly free from substances volatile in steam, yield a hard amorphous mass on cooling.² Alterna-

¹J. S. C. I. 1919, 187A; German Pat. 305,775, Feb. 13, 1917.

²Chem. Fabr. vorm. Weiler-ter Meer. Ger. Pat. 355,173, Feb. 3, 1920, and 355,174, Sept. 24, 1920; J. S. C. I. 1922, 41, 772A.

tively the cresol or the like may be saturated with chlorine at ordinary or slightly higher temperatures, and the resulting product heated above 100° C. under reduced pressure. The products, according to the chlorine content, are soluble in alcohol, acetone, ether, and alkalis. When the chlorine content is high the products are soluble only in hydrocarbons of the benzol type. They can be used for the preparation of dark or black varnishes and have a strong bactericidal action.

Benzyl Chloride Resins.

Resin-like substances are formed by treating compounds of the type of the benzyl halides, $R\cdot CH_2X$, (R = an aromatic residue, X = halogen) with metals or metal halides. Zincke³ permitted copper, silver and other metals to react on benzyl chloride. A resin, insoluble in all organic solvents, has been obtained by reacting on a mixture of benzyl chloride and carbon disulphide with aluminum chloride.

Benzyl Chloride and Copper.

Onufrowicz⁴ studied the reaction between benzyl chloride and copper by Zincke's method, obtaining a resin when he heated benzyl chloride and copper in a sealed glass tube at a temperature of 150 – 160° C. In order to investigate the reaction further he heated, in an open vessel at 150 – 160° C., equal quantities of benzyl chloride and copper for 2 hours. The reaction took place fairly rapidly with the separation of hydrochloric acid gas. Upon cooling, there remained a tough resinous mass which was slightly soluble in alcohol. The resin was soluble in benzol and upon evaporation of the benzol solution he obtained a tough, yellow, fluorescent product. The reaction proceeded just as well when the opening of the flask was closed with a calcium chloride tube so that only dry air entered. A thick liquid distilling between 110 – 360° C. was found just above the resinous layer. The distillate also solidified on cooling. However, on heating benzyl chloride and copper in equal parts to 100 – 140° C. in a dry atmosphere of carbon dioxide, hydrochloric acid was given off at 107° C. and when the reaction was complete a liquid product resulted.

Prost⁵ found that upon mixing zinc dust and benzyl chloride below the boiling point of the benzyl chloride he obtained a viscous product which could be distilled up to 340° C. Above this temperature a hard brown substance formed. He separated the distillate into three substances namely benzyl chloride, dibenzyl and toluol. The material boiling above 340° C. contains anthracene and a substance which appears to be identical with the hydrocarbon $C_{22}H_{18}$ found by Weber and Zincke.⁶

Soluble Resins from Benzyl Chloride.

Ferric chloride, acting on benzyl chloride in the cold, transforms the latter into a chlorine-free resin which is soluble in benzol and

³ Ber. 2, 739.

⁴ Ber. 1884, 833.

⁵ Ber. 1886, 875, Bull. soc. chim. 46, 247.

⁶ Ber. 7, 1154.

carbon tetrachloride.⁷ The reaction takes place without external heating. To 100 parts of benzyl chloride 0.5 part of anhydrous ferric chloride is added with stirring. Soon a vigorous evolution of hydrochloric acid begins and this progresses regularly for a considerable period. The temperature increases slightly. A dark brown, porous solid is formed, which is blown with steam to remove any unchanged benzyl chloride and is then ground and washed with hydrochloric acid to remove ferric chloride. A yellowish resin is obtained, soluble in benzol, carbon tetrachloride, chloroform, cyclohexanone, cyclohexanol acetate and various other vehicles but insoluble in alcohol. Solutions of the resin may be used for varnishing and the coatings are very resistant to acid and alkalis. Warm caustic soda solution of 40° B. does not attack the film. Resins also are obtained from benzyl bromide, orthochlor benzyl chloride and chlor methyl naphthalene.⁸

Benzyl chloride, benzal chloride, xylyl chloride and the like react, in the presence of iron, with naphthalene, anthracene, phenanthrene and various other coal-tar hydrocarbons yielding oils and resinous products.⁹

On heating benzyl chloride in a benzol solution with aluminum chips Radziewanowski¹⁰ found that in addition to diphenyl methane, a large quantity of tarry material was formed.

Benzal Chloride.

Halogenated aromatic hydrocarbons of the type $R.CHX_2$ yield resins when heated with phenols in the presence of a small quantity of a metal halide. Thus, benzal chloride is heated with either phenol, in the presence of zinc chloride at 50-100° C., or with m-cresol, in the presence of aluminum chloride at 70° C., until hydrogen chloride is no longer evolved, and the excess phenol or cresol is removed by steam distillation. An odorless, light-colored resin, which is soluble in caustic alkalis, methyl alcohol, ethyl alcohol, benzol, and chloroform is thus obtained. Similar products are obtained from homologues of benzal chloride or from derivatives containing halogen atoms in the nucleus.^{10a}

Xylol and Ethylene Chloride.

The careful heating of a mixture of xylol and ethylene chloride (sym) in the presence of aluminum chloride yields oily bodies. Stronger heating gives resinous substances.¹¹ To make a resin, equal parts of xylol and ethylene chloride are heated, with 2 or 3 per cent of aluminum chloride, to 100-150° C. under a reflux condenser. Hydrochloric acid is evolved and by absorbing the acid in a weighed amount of water a control on the progress of the reaction is

⁷ Badische German Pat. 280,377 and 280,595, Jan. 25, 1913; Chem. Z. Rep. 1914, 573; J. S. C. I. 1915, 500.

⁸ Instead of using ferric chloride in the cold, aluminum or zinc chloride may be used hot. German Pat. 280,595.

⁹ Bayer, German Pats. 301,713, Jan. 29, 1916; 302,531, Feb. 9, 1917.

¹⁰ Ber. 1895, 1135.

^{10a} Dynamit A.-G. vorm. A. Nobel und Co. German Pat. 355,389, Jan. 4, 1920; J. S. C. I. 1922, 41, 772A.

¹¹ Badische, German Pat. 326,729, June 9, 1918.

at hand. The mixture should be stirred during the reaction. The crude resin is washed and steamed to remove acid and unchanged xylol or ethylene chloride. The resin can be kneaded when hot but hardens on cooling.¹²

Chlornaphthalene Resin.

When heated with aluminum chloride, naphthalene tetrachloride is resinified and the resin obtained is soluble in benzol, turpentine and linseed oil, but insoluble in alcohol. The resin has been recommended for use in the preparation of varnishes and lacquers.¹³ It may be prepared by dissolving 100 parts of naphthalene tetrachloride in 400 parts of toluol, adding 3.5 parts of aluminum chloride and heating for several hours on a steam bath. The solvent then is expelled by distilling with steam and the resinous mass is heated to 150° C. to expel moisture. A clear brittle resin, soluble without residue in benzol, turpentine and linseed oil, is produced. Another procedure is to mix 100 parts naphthalene tetrachloride, 300 parts xylol and 3 parts ferric chloride, heating this mixture first on the water bath and then to 130° C. for several hours. The resin is similar to that obtained by the foregoing procedure. A crude chlorinated mixture likewise may be resinified. Thus 256 parts of naphthalene in 800 parts of chloroform are chlorinated until chlorine equivalent to about $3\frac{1}{2}$ atoms to the molecule of naphthalene has been taken up. The solution now contains di- and tetrachloride of naphthalene. 20 parts of aluminum chloride are added and the solution boiled for several hours to accomplish adequate resinification. Antimony pentachloride may be used as a catalyst. The reaction also may be carried out in the presence of naphthalene.¹⁴

Chlor Naphthalene and Phenols.

Resinous products soluble not only in benzol, chloroform, linseed oil, and turpentine, but also in alcohol, are prepared by the action of metal halides on a mixture of halogen addition products of naphthalene or its derivatives, or halogen derivatives of hydrogenated naphthalene, and phenols, in the presence or absence of solvents. Thus, phenol is heated to 90-95° C. with a solution of naphthalene tetrachloride in tetrachloroethane in the presence of ferric chloride; o-cresol is heated to 100° C. with a solution of naphthalene tetrachloride in o-dichlorobenzene in the presence of ferric chloride or aluminum chloride; or a mixture of phenol, ferrous chloride, and the product obtained by chlorinating tetrahydronaphthalene at ordinary temperature until

¹² By boiling tetraphenyl dichlor butene with alcoholic potash a small amount of resinous substance forms. Brand, Ber. 1921, 54B, 1987.

¹³ Actien-Gesellschaft für Anilin Fabr., German Pat. 332,391, Jan. 9, 1918.

¹⁴ Chlor naphthalenes are submitted, at 215° C., to the action of a current of air or neutral gas to remove constituents acting as skin irritants. Deutsche Conservierungs-Gesellschaft m.b.H.; J. S. C. I. 1921, 188A; German Pat. 327,704, 1917.

4 atoms of chlorine have been absorbed, is heated to 100° C. The products are washed free from acid and dried at 140-150° C.¹⁵

Chlorinated Tetrahydronaphthalene.

Chlorine is passed, at room temperature, into tetrahydronaphthalene until a weight increase equivalent to 2 atoms of chlorine to the molecule of tetrahydronaphthalene is observed. Five per cent of aluminum chloride (based on tetrahydro compound taken) is added and the mixture is heated to 200° C. On cooling a hard resin results. Thirty parts of the dichlor-derivative, obtained as above, are dissolved in 120 parts of toluol. One part of aluminum chloride is added and the mixture boiled under a reflux condenser for several hours. This procedure affords a semi-solid resinous material, the benzol solution of which dries to a varnish-like coating. Raw material of a more advanced stage of chlorination also may be used. Tetrahydronaphthalene, chlorinated to a weight increase corresponding to 3 or 4 atoms of chlorine to the molecule, is heated to 250° C. in the presence of 0.7 per cent ferric chloride. This treatment yields a brittle resin. Brominated derivatives of tetrahydronaphthalene are resinified in a similar manner.¹⁶

Hard resinous products have been obtained by treating benzene derivatives halogenated in the side chain, with phenols, naphthols or their derivatives in the absence of catalysts; the treatment being continued until evolution of hydrogen chloride ceases.¹⁷ Benzyl chloride yields oily products with phenol and alpha- or beta-naphthol, while both benzyl chloride and xylol chloride with salicylic acid yield viscous products which harden on standing.

Benzotrichloride and ortho cresol react with the formation, in part, of a yellow resin.¹⁸ Benzotrichloride also reacts with alpha-naphthol to yield an amorphous product insoluble in water, soluble in alcohol and benzol.¹⁹

Diphenylamine.

As a substitute for copal and for the resins used in sealing wax, Goldschmidt proposed the employment of a resin formed by heating methyl aniline or methyl diphenylamine with formaldehyde and hydrochloric acid for 2 hours and then oxidizing.²⁰

Benzylaniline Resin.

Goldschmidt's investigations led Herzog²¹ to experiment on the condensation of secondary amines in which a benzyl group forms one

¹⁵ A.-G. für Anilin-Fabr. German Pat. 334,710, Oct. 5, 1918, J. S. C. I., July 15, 1921, 479A. A mixture of tetrachloronaphthalene and asphalt has been used by Edison, U. S. Pat. 1,083,354, Jan. 6, 1914, as an insulating coating or varnish. Six parts of chloronaphthalene are mixed with 1 part asphalt.

¹⁶ The addition of iron or other metals as catalyst in the production of chloronaphthalenes to be used in making resins, diminishes the proportion of low-boiling, poisonous constituents in the product. Deutsche Konservierungs-Ges. m.b.H. German Pat. 332,725, April 11, 1920; J. S. C. I. 1921, 479A.

¹⁷ Kalle & Co. German Pat. 346,384, 1917; J. S. C. I. 1922, 510A.

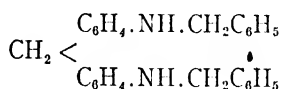
¹⁸ Schroeter, Ann. 257, 68.

¹⁹ Doebner, Ann. 257, 56.

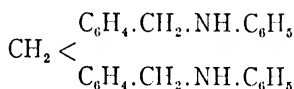
²⁰ Chem. Z. 1905, 33.

²¹ Oester. Chem. Z. 1921, 24, 16.

component. A resin was obtained by heating for one hour (under reflux condenser) 9 gms. benzyaniline, 10 gms. aqueous formaldehyde (40 per cent) 20 cc. water and 1 cc. hydrochloric acid. A 94 per cent yield of a brittle, brownish yellow, transparent resin was obtained. This product is probably a condensation of two mols. benzyaniline with one of formaldehyde to form dibenzyl-diaminodiphenylmethane.



and finally by rearrangement^{21a} yielding diphenyldiaminodibenzylmethane



The resin is easily soluble in benzol and trichlorethylene in the cold and dissolves in turpentine on heating. When the resin is prepared in alcohol as a diluting medium, the product exhibits a redder tone. Neither organic acids nor alkalies act as resinifying agents. The product differs from the resin obtained by Goldschmidt in that the reaction proceeds only to the formation of diphenylmethane derivatives, thus furnishing a stable resin suitable for use in the varnish industry while Goldschmidt's resin from methylaniline and methyldiphenylamine is a more complex product, subject to partial oxidation on exposure to air with the formation of strongly colored substances. Hence Herzog regards Goldschmidt's resin suitable only for sealing wax.

Ketene Imines.

The simple ketene imines, $\text{H}_2\text{C}:\text{C}:\text{NR}$, polymerize very rapidly. Ketene ethylimine, $\text{H}_2\text{C}:\text{C}:\text{N C}_2\text{H}_5$, polymerizes readily at room temperature. Ketene phenylimine, $\text{H}_2\text{C}:\text{C}:\text{N C}_6\text{H}_5$, also polymerizes with facility.²²

Cyanamide Compounds.

Acetyl cyanamide is a syrup which on heating is converted with explosive violence into a solid.²³ Isovaleryl cyanide acts similarly.

Dicyanamide.

Free dicyanamide cannot be isolated owing to the speed with which it is converted into an insoluble amorphous polymeride of high molecular weight.²⁴

Aniline and Formaldehyde.

Böhler²⁵ prepares a resin by heating anhydroformaldehydeaniline to a temperature of 130–140° C. for 10 to 12 hours. A dense cloud of white vapors is given off during the reaction. The presence of aniline during the distillation is

^{21a} Note German Pat. 58,072.

²² Staudinger and Hauser, *Helvetica Chim. Acta* 1921, 4, 887.

²³ Beilstein, 3rd. Ed., Vol. 1, 1438.

²⁴ Madelung and Kern, *Ann.* 1922, 427, 1; *J. Chem. Soc.* 1922, 122, i, 439.

²⁵ *Kunststoffe*, 1921, 118; 142; German Pat. 335,984, April 17, 1917.

desirable as it appears to facilitate the reaction and to improve the solubility of the resin in benzol or alcohol. Slight amounts of acids or alkalis may be added to the reaction mixture. This synthetic resin is said to have the property of increasing the solubility of difficultly-soluble natural or artificial resins and to otherwise improve their qualities. Soane^{26a} obtains a resilient composition for printers' rollers by treating a water-containing mixture of glue and glycerol with aniline-formaldehyde condensation products. In the course of preparation of anhydroformaldehydeaniline from aniline and formaldehyde Eberhardt and Welter²⁶ obtained some polymerized anhydro compounds and resinous bodies.

Methylene Diphenyldiamine and Phenol.

A semi-solid resin made from phenol and methylene diphenyldiamine is found by Achtmeyer^{26a} to be useful for impregnating brake linings. 100 parts by weight of phenol and 75-100 parts methylene diphenyldiamine are heated in an open vessel and stirred. Ebullition occurs, water is eliminated and a soft resin is obtained which hardens when heated with 7-10 per cent of paraform. Brake linings impregnated with this reaction mixture are baked at a temperature gradually rising to 400° C.

Naphthylamine Resins.

Acetaldehyde reacts with β -naphthylamine and with mixtures of α - and β -naphthylamine in the presence of solvents, e.g., benzol, to form a hard resinous compound and a product resembling Canada balsam respectively; the products are suitable for use in the manufacture of varnishes and tracing paper. A product resembling rosin can be prepared by treating a mixture of equal parts of α - and β -naphthylamine with formaldehyde; the mixture is agitated at 100° C., and, after cooling and separating the aqueous layer, the product is purified by kneading under hot water, and dried at about 120° C. A mixture of α -naphthylamine and xylydine also may be used.²⁷

Other Nitrogen Compounds.

Fischer and Luckmann obtained a brown resin in the preparation of triphenylpyrrolmethane derivatives.²⁸ Experiments on the condensation of pyrrole and N-methylpyrrole with formaldehyde and preparation of pyrrole glycols, conducted by Chelintzev and Maksorov²⁹ yielded transparent vitreous masses and resinous substances. In the preparation of p-nitrophenylhydrazine Davies³⁰ observed the formation of a diazo-sulphonate which separates as an unstable orange mass and readily decomposes with formation of a resin. During the study of tetraethylammonium and its compounds by Schlubach and Ballauf,³¹ a compound was obtained with dimethylpyrone which quickly resinified on contact with air to a brownish mass. The preparation of methylenediphenyldiimide is accompanied by the formation of a resin.³² Guanidine³³ in concentrated aqueous solution is energetically attacked by acetaldehyde yielding a resinous mass.

^{26a} U. S. Pat. 1,223,745, Apr. 24, 1917.

²⁶ Ber. 1894, 27, 1805.

^{26a} U. S. Pat. 1,429,267, Sept. 19, 1922.

²⁷ Farbzw. vorm. Meister, Lucius, und Brüning, German Pat. 300,685, Mar. 31, 1917; 303,953, Mar. 16, 1916; 305,026, Sept. 9, 1917; J. S. C. I. 1922, 41, 382A.

²⁸ Z. physiol. chem. 1921, 115, 77.

²⁹ J. Russ. Phys. Chem. Soc. 1916, 48, 748; Chem. Abs. 1917, 782.

³⁰ Chem. Soc. Trans. 1922, 121, 715; J. S. C. I. 1922, 41, 435A.

³¹ Ber. 1921, 54B, 2811, Chem. Abs. 1922, 16, 1391.

³² Eberhardt and Welter, Ber. 1894, 27, 1810.

³³ Mois Scientifique, 1903, 647; Rev. gén. chim. 1907, 54.

Quinoline, according to Williams³⁴ yields a solid resinous base on heating with sodium amalgam.³⁵ Resinous products have been obtained from certain derivatives of phenylindazole by Auwers and Hüttenes.³⁶

Phosphorates.

Resinous bodies are often obtained in the hydrolysis of cyclohexene phosphorates.³⁷ The phosphate of olive oil is an amber colored resin which is rather hygroscopic; in fact all of these products appear to be water absorbent.

When triphenylphosphamide is heated for several hours at 250-260° in air or carbon dioxide, aniline and water split off and a resinous polymer containing —N:P:N— as a resinophore group, is formed.³⁷

Chromium Compounds.

Peculiar resinous substances are obtained from some of the phenyl chromium compounds.³⁸ Pentaphenyl-chromium bromide was prepared by the reaction between phenyl magnesium bromide and chromium chloride (CrCl₃). It was obtained as an orange-brown amorphous powder or a viscous, foamy, lac-like mass, which could not be purified because of its amorphous properties and sensitiveness to light, air, heat and acids. The compound is soluble in many organic solvents. Mercuric chloride precipitates from alcoholic solution a mass resembling sealing wax, which is insoluble in organic media.

Naphthalene Formaldehyde Resin.

The treatment of naphthalene with more than one half an equivalent of formaldehyde in the presence of sulphuric acid affords a resin soluble in benzol and homologues but insoluble in alcohol, turpentine and linseed oil. Bohn³⁹ has given a number of procedures for making resins of this type.

Naphthalene, 10 parts, is added to 30 per cent formaldehyde, 8 parts admixed with 97 per cent sulphuric acid, 115 parts. The temperature is raised to 100° C. and held at that point, cooling if necessary, for about 1½ hours, when the mixture becomes thick. Hot water is added and the resinous mass is cooled, pulverized and washed to remove acid. The resin may be purified by dissolving in benzol and adding a small quantity of alcohol to precipitate unchanged naphthalene. Another procedure is to add 10 parts of naphthalene to a mixture of 7 parts of formaldehyde (30 per cent) and 10 parts sulphuric acid (97 per cent). Heat to 120-140° C., with stirring, until a viscous paste has formed. This may be purified in the same manner as the foregoing. Or use 10 parts of naphthalene to 14-16 parts of formaldehyde and 20-23 parts sulphuric acid, the temperature being held at 130° C. until a viscous mass results. The crude material

³⁴ Chem. News 43, 145; J. Chem. Soc. 1881, 40, 613.

³⁵ Note also Williams, Jahresber. 1878, 891, and Claus, Ber. 1881, 14, 1939.

^{36a} Ber. 1922, 55B, 1112; Chem. Abs. 1922, 16, 3655.

³⁷ Willstätter and Sonneckfeld, Ber. 47, 2801.

³⁸ Herzog. Oesterr. Chem.-Ztg. 1921, 24, 76; Chem. Abs. 1922, 16, 1671; S. C. I. 1921, 478A; J. Chem. Soc. 1921, i, 519. See Chap. 13.

³⁹ Hein, Ber. 1921, 51B, 1905.

⁴⁰ Badische, U. S. Pat. 898,307, Sept. 8, 1908.

can be purified by solution in benzol, shaking the solution with milk of lime or carbonate of soda and precipitating the clear solution with alcohol. Methylal may be used in lieu of formaldehyde. The purified resin is a yellow-brown glossy material. Halogen substituted derivatives of naphthalene likewise resinify in the presence of acids. From α chlornaphthalene there are obtained clear elastic resins, soluble in benzol, chlorbenzol, fatty oils or turpentine, and suitable for use in varnishes and for the preservation of leather.⁴⁰

Bayer & Co.⁴¹ treat hydrocarbons with formaldehyde or substances yielding formaldehyde in the presence of sulphuric acid of concentration below 60 per cent. For example if naphthalene is heated to 110-115° C. with 40 per cent formaldehyde and sulphuric acid (66° B., sp. gr. 1.84) a white resin is obtained which is soluble in acetone, benzol, solvent naphtha, carbon tetrachloride and carbon disulphide. Phenanthrene gives under the same conditions a brownish-yellow, brittle resin soluble in benzol and xylol, anthracene a yellow resin soluble in benzol. Benzol heated under pressure to 118-125° C. with 40 per cent formaldehyde and 96 per cent sulphuric acid gives a soft brown resinous mass soluble in benzol. Toluene gives a clear liquid soluble in ether, acetone, benzol, chloroform, and carbon tetrachloride. Xylol heated for six hours with 40 per cent formaldehyde and 96 per cent sulphuric acid gives a brown resin soluble in acetone, benzol, carbon tetrachloride, and solvent naphtha. The products melting below 100° C. are of value in the varnish industry.

Condensation products of naphthalene with formaldehyde, suitable for use in the lacquer or varnish industry, are prepared by Folchi⁴² as follows: 100 grams of naphthalene are added to 80 cc. of 30 per cent formaldehyde, 100 cc. of sulphuric acid (66° B., sp. gr. 1.84) gradually added, and the mixture heated under a reflux condenser on a water bath at 80° C. for 1½ to 2 hours with agitation. The contents of the flask are poured into water at 80-90° C. and the melted condensation product washed with water, dilute alkali, and water again. The mass is then dried at 80° C. for 4 to 5 hours. For use as lacquer the material is melted with a small quantity of turpentine and mixed with refined tar. By strict attention to the above reaction conditions a weight yield of 100-110 per cent of the naphthalene used may be obtained. The hardness of the product varies with the temperature of formation. If the condensation product is granular this can be rectified by melting with turpentine and then washing with water. If the acid is not completely removed the mass will not dry satisfactorily. An alternative method is to use 100 grams of naphthalene, 80 grams of 40 per cent formaldehyde, and 120 grams of sulphuric acid, heating for 3 hours at 90-95° C.; in this case the yield is 80-90 per cent.

⁴⁰ See also German Pat. 207,743, 1907; British Pat. 16,245, July 15, 1907; French Pat. 336,664, 1908; Norw. Pat. 26,692, 1916; German Pat. 332,334, 1918; J. S. C. I. 1908, 457, 695; 1909, 431, and 1913, 876; Chem. Abs. 1916, 1586.

⁴¹ J. S. C. I. 1922, 41, 630A; German Pat. 349,741, 1918.

⁴² Chem.-Z. 1922, 46, 714; J. S. C. I. 1922, 41, 720A; Chem. Abs. 1923, 216.

Hydrogenated Naphthalene and Formaldehyde.

Hydrogenated naphthalene is treated with formaldehyde in the presence of acids, with or without the addition of a solvent or diluent. Resinous products are obtained which can be worked up with turpentine and linseed oil for the manufacture of varnishes.⁴³

Naphthalene Condensation.

A resinous condensation product is obtained by heating naphthalene with glycollic acid or glycolide and an acid reagent such as phosphorus pentoxide. Thus a mixture of 120 parts of naphthalene, 40 parts of glycollic acid (or 30 parts of glycolide), and 10 parts of phosphorus pentoxide, is heated under pressure for about 15 hours at 130-170° C. with agitation. Carbon dioxide is allowed to escape from the apparatus from time to time. The product, after separation of unchanged naphthalene by steam distillation, is a yellow resin resembling shellac and fusing at 80-85° C.⁴⁴

The product obtained by treating 60 parts of naphthalene with 320 parts of bromine at 100° C., on heating at 150° C. under pressure for 6 hours with sodium hydroxide and methyl alcohol, yields a resinous mixture of polybromohydroxynaphthalenes.⁴⁵

Naphthalene and Sulphuric Acid.

Weissgerber and Kruber⁴⁶ have found that if crude naphthalene is freed from all accompanying oil by pressing and treated with an amount of concentrated sulphuric acid insufficient for complete sulphonation at 90-100° C. considerable resinification occurs. If the amount of sulphuric acid is small (8-10 per cent of the crude naphthalene), only a small part of the naphthalene is converted into its sulphonic acids.

Resinification of Turpentine and Pine Oil.

By simply treating turpentine or pine oil with a polymerizing agent, 92 per cent sulphuric acid, at a temperature of 80-160° C., Gardner obtains a paint vehicle, which dries to a firm surface. 5-7.5 parts of the acid are used to 100 parts of the oil.⁴⁷ Orloff⁴⁸ reacts on turpentine with formaldehyde in the presence of sulphuric acid to obtain a resin. The procedure is as follows:

⁴³ A.-G. für Anilin-Fabr., German Pat. 305,575, Apr. 19, 1917; J. S. C. I. 1921, 439A.

⁴⁴ Elektrochem. Werke G.m.b.H. Bosshard, and D. Strauss, British Pat. 171,956, Jan. 10, 1921; J. S. C. I. 1922, 41, 676A.

⁴⁵ Akt.-Ges. f. Anilin-Fabr., German Pat. 349,794, July 29, 1914. Addn. to 281,175; J. S. C. I. 1922, 41, 688A.

⁴⁶ Ges. f. Teerverwertung m.b.H. Duisburg-Meiderich, Ber. 1920, 53B, 1551; Chem. Abs. 1921, 15, 88.

⁴⁷ U. S. Pat. 1,370,106, March 1, 1921.

⁴⁸ J. Russ. Chem. Soc. 1908, 40, 800; German Pat. 191,011, June 14, 1906.

(1) To 100 parts by weight of turpentine add drop by drop 200 parts of 66° sulphuric acid. The temperature should not exceed 40° C.

(2) Add 55 to 66 parts formaldehyde (40 per cent. solution); the temperature still being held below 40° C.

(3) Allow to remain for 12 hours at ordinary temperature then neutralize with aqueous ammonia until the color becomes greenish.

(4) Cool and remove ammonium sulphate liquor. Treat again with ammonia, heating to boiling. The color changes to yellow or reddish-yellow.

(5) Collect the resin, wash with boiling water, press and dry at 70-80° C.

The resulting product is a brownish red resin partially soluble in alcohol, benzol, toluol, glacial acetic acid and ether. To transform this product into a soluble one the resin is heated in a distilling apparatus. Strong frothing occurs between 110-150° C. Further heating to 290° C. yields a brownish black hard resin soluble in benzol, toluol, glacial acetic acid and ethyl acetate. It is, however, only partially soluble in alcohol and petroleum ether. The resin yield is 80-83 per cent on the weight of the turpentine. Varnish coatings made from this resin are very flexible.

Pine Oil and Paraform.

In like manner reaction takes place between ordinary pine oil and paraform, forming dark colored resins. The following experiment was performed in the author's laboratory. 50 grams of pine oil, 15 grams of paraform and 20 cc. of concentrated hydrochloric acid were admixed and the mixture was heated under a reflux condenser. After the paraform had passed into solution an additional quantity of 15 grams was added and the refluxing continued. This also went into solution but the odor of formaldehyde persisted. The oily reaction product became very dark brown in color and considerably thicker. The reaction product did not separate easily from the aqueous acid hence was extracted with benzol. After evaporation on the water bath a product of tarry consistency remained. When this was carefully heated to a somewhat higher temperature a portion volatilized and the remainder upon cooling solidified to a brittle brownish black mass.⁴⁹

Indene and Formaldehyde.

Acids serve as a condensing agent in bringing about reaction between indene and formaldehyde. The condensation product is viscous when cold and becomes a thin liquid on heating. It has the property of drying on exposure to air, thus serving as a varnish.⁵⁰ To make the resinous material 5 to 10 kilos of concentrated hydrochloric acid are mixed with 100 kilos each of indene and 30 per cent formaldehyde solution. This mixture is boiled 5 hours under reflux condenser until the indene disappears and a thick clear oil collects at the bottom. The oil is separated from the aqueous portion and is washed with sodium carbonate solution, then dried.

⁴⁹ Rietz describes a product, suitable for therapeutic purposes, derived from cholic acid and paraform. U. S. Pat. 1,213,261, Jan. 23, 1917.

⁵⁰ Claasz, German Pat. 310,783, Feb. 19, 1918.

Pyranhydrones.

Phenol ethers reacting with acetic anhydride in the presence of catalyzers are substituted in the nucleus. On treatment with an alkali a dark blue resinous mass separates which is soluble in alcohol, benzol and chloroform. Other resinous or amorphous substances are obtained by reacting on this product with hydrochloric acid, etc.⁴¹

Brom camphor, treated with butyric ester in the presence of magnesium gives a resin. Acetyl chloride and bromide behave similarly.⁴² While esterifying alcohols and phenols Hauben⁴³ found that unsaturated alcohols like geraniol linalool and terpineol yield colored esters, with magnesium alkyl bromides, which quickly become resinous.⁴⁴ Tropinonecarboxylic acid ester is an oily substance which hardens when exposed to air.⁴⁵

Essential Oil Resinification.

Grognot⁵⁶ has described synthetic resins prepared by adding phosphoric anhydride to essential oil of sweet almonds in sufficient quantity to make a syrupy mass. If care is taken to avoid a rise in temperature the mass turns a yellowish brown color and becomes hard at ordinary temperature in a few days. The product is then washed with hot water; the excess of essential oil is expelled on the water-bath, and a resin obtained which is soft when hot, brittle when cold, odorless, and having the appearance of colophony. This is purified by dissolving in alcohol and precipitating with water acidulated with hydrochloric acid. The resin has a composition identical with that of the α -resin of benzoin. It is only partially soluble in ether. From solution in alcohol it is precipitated by an alcoholic solution of acetate of lead.

If phosphoric anhydride is added to eugenic acid until it acquires the appearance of turpentine, the mixture turns red, and when exposed for some hours to a temperature of 50° to 80° C. it becomes dark red in color and very hard. After washing with hot water, the resin is dissolved in alcohol and precipitated with acidulated water. Eugenic resin is odorless, has the appearance of colophony and an aromatic and bitter taste. In the preparation of the resin, if an excess of phosphoric acid is used, a combination containing phosphoric acid is formed, from which the resin may be extracted by proper treatment. The composition of this resin is intermediate between eugenic acid, $C_{10}H_{12}O_2$, and a body of which the formula is $C_{10}H_{12}O_3$. On dry distillation it yields an oil with the odor of creosote, a part of the resin being carbonized. Essential oil of rue forms a deep brown resin, which melts imperfectly with potassium hydrate. The stearoptene of the essential oil of anise, $C_{10}H_{12}O$, treated with iodic acid and iodine with the addition of potash, is transformed at a moderate heat into a brown resin of which the composition differs little from the

⁴¹ Schneider and Meyer, Ber. 1921, 54B, 1484.

⁴² Malmgren, Ber. 1903, 36, 2639.

⁴³ Ber. 1906, 1736; J. Chem. Soc. 1906, 520.

⁴⁴ In the presence of sulphuric acid benzyl benzoate forms a white solid.

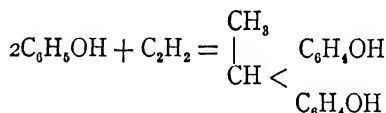
⁴⁵ Willstätter, Wolfes and Maeder, U. S. Pat. 1,419,091, June 6, 1922.

⁵⁶ Rev. gén. chim., 10, 49; Chem. Abs. 1907, 1179; J. S. C. I. 1909, 31.

stearoptene, except that it contains a little more oxygen. This resin melted with potash produces only a little of a crystalline substance which seems to be anisic acid.⁶⁷ Barth has carried out researches on oil of turpentine, lavender and juniper. These oils were treated with alcoholic potash, and the resultant deep yellow liquid evaporated in a water bath, the residue treated with dilute sulphuric acid, and digested in ether. The ether being distilled off, there remained a resinous body. After being acted on 3 or 4 hours by potash, the essential oil was found to be transformed into a hard, brittle resin resembling colophony. Camphor also produces resin, and this is always found in slight quantity in the preparation of camphoric acid by Berthelot's method. The camphor product is a golden-yellow resin, quite inodorous after having been heated to 100° C. It remains soft like pitch for a long time. The resins of turpentine and of lavender appear to be $C_{20}H_{30}O_3$; that of camphor, $C_{20}H_{30}O_2$. The resin of turpentine is attacked with difficulty by potash and is only slowly oxidized. The products of oxidation are the lower fatty acids and of a composition analogous to camphoresinic acid.⁶⁸ The suggestion has been offered that the tannins are related to the resins, since their products of decomposition are often resinous.

Acetylene and Phenol.

The studies by Nieuwland⁵⁹ on the reactions of acetylene with phenol have yielded resinous bodies of great interest from an industrial standpoint. Nieuwland reacted on phenol with acetylene in the presence of concentrated sulphuric acid and a very small amount of mercury sulphate serving as a catalyst. This reaction mixture especially in solution in alcohol yields ethylidene diphenyl. The reaction is as follows:



The reaction with acetylene and catalyst in glacial acetic acid or without solvent proceeds with the formation of a fusible resin. Cresols form compounds similar to the phenol derivatives. Alcohol or acetone may be used as a solvent for phenol in place of glacial acetic acid. The acetylene in excess is passed through the phenol solution and catalyst, the temperature being finally raised to 50-120° C. and the pressure also being increased. The resin obtained may be rendered insoluble and infusible by heating with hexamethylenetetramine.⁶⁰

⁶⁷ Ann. 139, 83, 1866.

⁶⁸ Bull. soc. chim., 1868, 70.

⁵⁹ Private communication from Dr. J. A. Nieuwland, University of Notre Dame, Notre Dame, Ind. Note British Pat. 183,830, 1922; Chem. Abs. 1923, 218, Shawinigan Laboratories, Ltd.

⁶⁰ Chem. Age, London, 1922, 7, 537. A method of making acetaldehyde from acetylene by a continuous process involving the employment of a large excess

It has been ascertained that a reaction takes place between acetylene and o, m or p cresol in the presence of acids and of a mercury salt acting as catalyst, leading to the formation of resinous substances, while at the same time other bodies are produced which according to Melamid⁶¹ can be converted into tanning materials.

If acetylene is admitted for a considerable period of time into a mixture of cresols in the presence of sulphuric acid and a mercury salt acting as catalyst and the mixture then is submitted to vacuum distillation, a distillate having a high boiling point and which is completely soluble in water when sulphonated, and precipitates glue in aqueous solution, is obtained; together with a residue which consists of a hard, transparent, light-colored resin soluble in alcohol and benzol.

It appears that at first the acetylene combines with the cresol forming a cresol derivative, the condensation of which gives rise to a liquid having a high boiling point and hard substances of a resinous character. Melamid gives the following procedure.

100 parts by weight of commercial cresol are added with cooling to about 20 parts by weight of 50 per cent sulphuric acid, $2\frac{1}{2}$ parts by weight of mercury sulphate and one-half part by weight of ferric chloride. Acetylene is admitted with stirring for a period of about 12 hours as a slow current and at room temperature. The viscous product is dissolved in benzol, separated from the catalyst and sulphuric acid by means of filtration and washing with water, dried and submitted to fractional distillation under a pressure of 8 m/m. Up to 100° C. cresols pass over together with benzol, and between 100° and 200° C. the liquid product is obtained. The residue solidifies to a hard, transparent, yellow, odorless resin.⁶²

Acetylene and steam when passed over bog iron ore at 350° C. yield a mixture of higher aldehydes, acetone, furfuran derivatives, phenols and resinous substances.⁶³

According to Lilienfeld⁶⁴ alkyl, aryl, or aralkyl ethers of cellulose, starch, dextrin or other carbohydrates or their derivatives are mixed with the viscous oily liquids obtained when acetylene reacts in the presence of aluminum chloride with hydrocarbons (B.P. above 140° C.) occurring in tar oils, yielding plastic bodies.

Resinous Condensation Products from Aromatic Hydroxy-carboxylic acids.

Mixtures of different aromatic orthohydroxycarboxylic acids, e.g., of the three isomeric cresotinic acids, or of salicylic acid and meta and paracresotinic acids, are heated with the usual acid condensing agents such as phosphorus oxychloride, acetyl chloride, acetic anhydride, car-

of acetylene to carry the acetaldehyde away from the zone of the reaction, thereby avoiding the formation of acetaldehyde resin, is described by Matheson, *Chem. Age*, New York, 1922, 464.

⁶¹ British Pat. 163,679, Nov. 26, 1920.

⁶² Note also *Chem. Age*, London, 1922, 6, 22.

⁶³ Stuer and Grob, U. S. Pat. 1,421,743, July 4, 1922.

⁶⁴ *Chem. Abs.* 1921, 15, 419; British Pat. 149,319, May 14, 1920.

bonyl chloride, and sulphuryl chloride, whereby resins are obtained which are completely soluble in acetone, benzol, amyl acetate, paraldehyde, solvent naphtha, tetrahydronaphthalene, and linseed oil. When applied to metal, wood, etc., such solutions produce a hard, glossy surface which is resistant to chemical reagents and to light, air and water.⁶⁵

Lead Oxide and the Phenols.

A curious type of resin which has been extensively investigated by Fischer and Ehrhardt⁶⁶ is that obtained by reacting on a phenol with lead oxide (litharge) to obtain a basic compound. Lead oxide dissolves readily in phenol with a strong evolution of heat and on cooling a gelatinous mass results. In water a basic lead phenolate separates. When this basic salt is heated above 100° C. a viscous product is obtained which may be drawn into threads and on cooling yields a glassy mass. The properties of the compound attracted the attention of Fischer and Ehrhardt and an attempt was made to utilize products of this character in the production of varnishes and paints. The coatings of the resinous material are not very hard but are brittle and on protracted exposure show indications of formation of lead oxide at the surface. The resin prepared from phenol itself when applied as a coating to a surface will crystallize in the course of a few days and become worthless. Lead oxide likewise combines with cresol, parahydroxydiphenyl and the naphthols. The higher the molecular weight the less is the tendency to crystallize, and quite durable coatings were obtained by Fischer and Ehrhardt from lead oxide and alpha naphthol. Phenols from the crude phenol-rich fraction (middle oil) of low-temperature tar or coke oven tar yield products which have been found useful for protecting ironwork from rust.

In preparing the lead compound, lead oxide should be added to the phenol at about 120° C., the additions being made in small portions and with strong agitation, as the resinous compound is decomposed by overheating. The product may then be thinned with benzol or solvent naphtha or the diluent (of sufficiently high boiling point) may be present during the reaction. The amount of lead oxide added should be sufficient to give the basic compound.

Ordinary phenol, 4.7 parts, and lead oxide, 10.8 parts, yielded a solution which gave a glassy coating on drying but in two days was cloudy, becoming crystalline and powdering readily. A cresol mixture known as liquid carbolic acid, 5 parts, with lead oxide, 10.8 parts, yielded a coating which became crystalline in the course of a few days. Parahydroxydiphenyl, 8.5 parts, and lead oxide, 10.8 parts, gave a good coating which was unchanged for months. Alpha naphthol, 7.2 parts, and lead oxide, 10.8 parts, yielded a varnish the coating of

⁶⁵ *Farbw. vorm. Meister, Lucius, and Brüning*, German Pat. 344,034, March 26, 1920; *J. S. C. I.* 1922, 47, 301A.

⁶⁶ *Ges. Abhandl. Kennt. Kohle*, 1919-1920, 4, 257, 264; *Chem. Centr.*, 1920, 92, II, 854; *J. S. C. I.* 1921, 398A.

which was slightly greenish in color after drying. The coating showed no tendency to crystallize and appeared quite resistant to weathering influences. Beta naphthol did not give as hard a product but did not crystallize. Phenolphthalein was unaffected by lead oxide.

Phenols from low temperature tar (b.p. 200-270° C.) 200 cc., lead oxide, 125 grams, heated to 120° C. reacted violently and the temperature rose to 140° C. The compound finally was heated to 155° C. and subsequently thinned with 150 cc. of benzol. A rather durable varnish was obtained. Phenols boiling between 200-250° C. similarly treated with lead oxide gave a matte varnish which did not crystallize.

However, none of these products is particularly satisfactory either for preparing varnishes or paints, and from such investigation as the author has made there appears to be little chance of any extensive use of these lead compounds in ordinary varnishes and paints. Possibly in anti-fouling paints or in molding compositions where high density is of importance the phenolates of lead could be used as a binder. The basic compounds of lead with the phenols are relatively very heavy substances. Because of this, perhaps they may have a field of application in weighting or loading fibrous material.

Pressure Oxidation of Coal Tar.

Low-temperature coal tar and also the fraction distilling below 270° C. were subjected by Fischer and Ehrhardt to pressure oxidation in a continuous stream of air at 150° C. and 40 atm. pressure. The results left it uncertain whether the hydrocarbons as well as the phenols were oxidized. The product was a black lustrous pitchy product partly soluble in benzol. The oxidation product of the hydrocarbons separately treated contained a clear, limpid oil and also a reddish yellow oil which deposited solids when cooled, and dried in air like varnish. The hydrocarbons thus were attacked, although to a lesser extent than the phenols. In an experiment on the oxidation of the tar fraction up to 270° C., the hydrocarbons were scarcely attacked at 100° C., whereas the phenols were extensively changed into resins and acids. Lead oxide was found to have no catalytic effect, and the experiment throws light on the behavior of lead phenolate paints. The lead phenolate, partly by hydrolysis and partly by the action of carbon dioxide, is slowly decomposed, forming free phenol, which is slowly oxidized. It seems probable that the oxidation products of low-temperature tar are suitable for use as paints and varnishes.⁶⁷

Pressure Oxidation of Phenols.

A more extensive investigation of oxidation of phenols to resins was made by Fischer and Schrader.⁶⁸ The oxidation was carried out using air under 45 atmospheres pressure. The investigators were

⁶⁷ Ges. Abhandl. Kennt. Kohle, 1919, 4, 280; Chem. Abs. 1921, 15, 2713.

⁶⁸ Ges. Abhandl. Kennt. Kohle, 1919, 4, 293; Chem. Centr., 1921, 92, 11, 606; S. C. I. 1921, 340A.

seeking to obtain substances similar to Bakelite from the phenols of low-temperature tar without the use of formaldehyde. The products obtained were partly insoluble condensation bodies and partly degradation products.⁶⁹ Under some conditions fairly clear resinous substances were obtained, the color being dependent on the reaction and concentration of the original mixture. Phenol at 100° C. in presence of a 2.5 N soda solution yielded a considerable quantity of brown resinous product, but less at 150-200° C. The three isomeric cresols were oxidized in presence of soda solution and ortho-cresol in presence of an excess of sodium hydroxide. Coloring matters and degradation products were obtained, but little resinous matter. The coloring matters were apparently fuchsine derivatives resulting from condensation of cresol and aldehydes. In presence of N/1 H₂SO₄ above 150° C. ortho-cresol was extensively oxidized, yielding solid substances. At 150° C. the products were a hard, lustrous orange-colored resin, soluble in benzol and alcohol, a brown substance insoluble in benzol and small quantities of coloring matter.⁷⁰ Fischer and Schrader sought to oxidize phenol to oxybenzyl alcohol, thinking thereby to derive dioxydiphenyl methane with resulting resinification. There is no evidence that the reaction takes such a course.

A method of making resinous substances from cresols or xylenols by oxidation with air or oxygen is carried out by Chemische Werke Grenznach A.G.^{70a} by passing a current of moist air through the raw material, for example, orthocresol at 150-170° C., for a period of 10 to 12 hours. A small amount of manganese dioxide or ferric chloride is present during the oxidizing treatment. Phenolic bodies which are not acted upon are driven off by distillation in a current of steam. The resulting resinous material varies in quality according to the duration

⁶⁹ Fischer, Gluud, and Breuer (Ges. Abhandl. Kennt. Kohle, 1919, 2, 222; Chem. Centr., 1919, 90, IV, 934) heated low-temperature coal-tar and various fractions of coal-tar, e.g., the fractions boiling below and above 300° C., the phenolic constituents, and the tar deprived of phenolic substances, under pressure in contact with "steel wool" in an autoclave at 320° C. for two successive periods of 3 days each. After this treatment the tar itself, and the hydrocarbons contained in it, showed a higher viscosity and density and a higher setting point than before. The phenolic constituents thickened more rapidly and to a greater extent than the hydrocarbons, giving products resembling pitch or asphalt.

⁷⁰ Phenol, or ortho-cresol, is caused to react with oxygen or gases containing oxygen at pressures higher than atmospheric pressure, in the presence or absence of aqueous alkali or acid and with or without a catalyst such as finely-divided iron, the procedure yielding resinous or asphalt-like condensation products. (Fischer, British Pat. 149,979, Aug. 10, 1920; J. S. C. I. 1922, 41, 22A.) Artificial resins are obtained by subjecting phenol or its homologues to moderate oxidation, e.g., by potassium ferricyanide, or by ferric chloride. By the action of alkalis, acids or heat, the brown products so obtained are rendered soluble in alkali or are further polymerized; by reduction, colorless products are obtained which are rendered insoluble in alkalis by alkylation or acylation. The products are soluble in benzol, ether, etc., to viscous colloidal solutions. (Pummerer, British Pat. 165,408, June 22, 1921; Chem. Abs. 1922, 16, 506.) Note also the comments of Herzog and Kreidl, Z. angew. Chem. 1922, 35, 643.

^{70a} German Pat. 357,756; Chem. Met. Eng. 1923, 28, 33.

of the oxidation treatment and the temperature. The products usually are dark brown to black masses which range in consistency from soft products to hard and brittle resins. The softer products are converted into highly lustrous hard and brittle resins on further heating. The resins are soluble in dilute caustic soda solution but are not soluble in a solution of sodium carbonate. They dissolve readily in various organic solvents such as ether, alcohol, acetone and benzol but are insoluble in cold turpentine. The soft resins are readily soluble in fatty oils but the hard resins go into solution very slowly. The resinification is supposed to be brought about by oxidation of the alkyl groups of the phenols and subsequent polymerization of the resulting intermediate reaction products; this second reaction occurring either between the intermediate products themselves or with unchanged phenols.

Bartoli and Papsoli¹¹ when electrolyzing solutions of phenol in potassium and sodium hydroxide, and using electrodes of coke, graphite, and platinum, obtained an acid having the composition $C_7H_6O_4$, which melted at 93° C. When retort coke was used as the positive electrode, an extensive decomposition of the phenol occurred and a resin was formed.¹²

Naphthalene Oxidation.

Naphthalene is electrolytically oxidized to α -naphthaquinone, with the formation of small quantities of phthalic acid and dark brown, resinous matter, in acid solution, using lead peroxide and platinum as the positive pole. This change does not occur in alkaline solution. The resinous substance contains phenolic hydroxyl groups and yields phthalic acid and an insoluble black substance when fused with potassium hydroxide.¹³

Dihydro naphthol treated with sulphuric acid gives an acid, the sodium salt of which contains resinous material.¹⁴

Phenolphthalein.

The exposure of phenolphthalein to a temperature of 250 – 253° C. yields a colorless melt which solidifies at about 217° C. to a glass-like mass.¹⁵ This observation has been confirmed by Herzog and Kreidl.¹⁶ The resin obtained was found to be soluble in dilute caustic soda solution and, on the addition of dilute acid, phenolphthalein in crystalline form was recovered. The glass-like product appears to be simply a polymer. Herzog and Kreidl explain this polymerization on the ground of desmotropic change.

Quinones.

Zincke¹⁷ found that a few quinones such as benzo-quinone and tolu-quinone react in alcoholic or acetic acid solutions with phenylhydrazine. On dilution with water of the slightly colored solution a resinous, oily substance separates which had not been previously investigated. Zincke¹⁸ states that if ammonia

¹¹ Gazz. Chim. 1884, 14, 103.

¹² Franke has obtained resinified phenolic compounds in the refining by oxidation of motor spirit from the cracking of peat tar. British Pat. 13,361. June 7, 1913; Ellis, Hydrogenation of Oils, New York, 1919.

¹³ Ono; J. Chem. Soc. Japan, 1921, 42, 38; J. Chem. Soc. 1921, 120, i. 334.

¹⁴ Rowe and Levin, J. Chem. Soc. 1921, 119, 2021; Chem. Abs. 1922, 16, 927.

¹⁵ Erdmann, Org. Präparatenkunde 1894, 327.

¹⁶ Z. angew. Chemie 1922, 35, 641.

¹⁷ Ber. 1883, 1563.

¹⁸ Ber. 1883, 1556.

is allowed to react with quinone in a dry ethereal or chloroform solution, he obtains besides hydroquinone and quin-hydrone, a brown amorphous substance. Thymoquinone exposed to light in ethereal solution forms polythymoquinone.⁷⁹

Synthetic Japanese Lac.

Morgan⁸⁰ refers to certain tests made by the Air Ministry on Japanese lacquer. Aircraft propellers coated with this lac were spun at high speed when exposed to a spray of water. The results showed the coating to be far more durable under this severe treatment than any ordinary varnish or paint coating. However, Japanese lacquer hardens only when exposed to a moist atmosphere and this condition is a serious drawback to its use. The investigations of Majima and his collaborators, begun in 1907, have an interesting bearing on the subject of synthetic resins. Majima⁸¹ in 1915 synthesized 2,3-dimethoxy-1-n-pentadecylbenzene, $(\text{CH}_3\text{O})_2\text{C}_6\text{H}_3(\text{CH}_2)_{14}\text{CH}_3$, and showed it to be identical with hydro-urushiol dimethyl ether which he had previously obtained by reducing and methylating "urushiol," the chief ingredient of Japanese lac. Majima and Takayama⁸² have compared the phenomena observed on oxidizing the monomethyl ether of urushiol with those observed when its lowest homologue, viz., 2-hydroxy-m-tolyl methyl ether, is similarly treated, and so conclude that the oxidation of hydro-urushiol yields derivatives of diphenoquinone.

Later work by Majima⁸³ appears to establish the fact that urushiol is a mixture of compounds differing from each other only in the number and positions of double bonds occurring in the long normal carbon chain, thus showing a marked similarity to the drying oils and making a quantitative separation of the components a practically hopeless task by our present chemical methods. All these components on reduction yield the same hydrourushiol and Majima therefore retains the name urushiol for the original mixture and assigns to it the average molecular formula $(\text{HO})_2\text{C}_{16}\text{H}_{27}$.

In the opinion of Morgan there appears to be an unnecessary amount of time and energy devoted to the possible production of synthetic resins intended merely to replace the natural "gum" in oil varnishes. He particularly calls attention to the need of a varnish which, when applied and allowed to dry in the usual manner, will yield a coating far more durable and resistant than any varnish now made from the usual varnish constituents of linseed oil, Chinese wood oil, etc. A product somewhat resembling Japanese lac, which could be produced in a commercial way synthetically and which preferably could be applied in the liquid condition at ordinary temperature, without the use of a volatile solvent, represents an ideal still far from attainment.

⁷⁹ Meyer-Jacobson, 1902, Vol. 2, Part 1, 446; Herzog and Kreidl, Z. angew. Chem. 1922, 35, 643.

⁸⁰ Reports of the Progress of Applied Chem. 1921, 6, 346.

⁸¹ Ber. 1915, 48, 1606.

⁸² Ber. 1920, 53, 1907.

⁸³ Ber. 1922, 55B, 172, 191; Chem. Abs. 1922, 2330; note also 1921, 63.

Isatin.

When isatin ⁸⁴ $\text{C}_6\text{H}_5\text{C} \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} > \text{CO}$ is allowed to act upon an aqueous solution

of resorcinol in the presence of an alkaline condensing agent until its color is discharged, a colorless, infusible substance is obtained, insoluble in the ordinary solvents, and apparently of high molecular weight.

Lignic Acid.

According to Fuchs ^{84a} lignic acids obtained by alkaline treatment of vegetable materials are converted into resin-like substances by the action of oxidizing agents, e.g., chlorine. The products obtained by the action of halogens on the lignic acids derived from straw are readily soluble in acetone, and amyl acetate, and form a hard, tenacious, lustrous surface after evaporation of the solvent.

Shellac and Tannic Acid.

Resins which are soluble in dilute alkalis, such as shellac, copal and phenol-formaldehyde condensation products when precipitated from alkaline solution by tannic acid, according to McCoy ⁸⁵ form plastic masses which may be molded in the cold. Shellac is dissolved in a 5 per cent aqueous solution of borax or sodium hydroxide and tannic acid added sufficient in amount to precipitate the shellac and form an alkali metal tannate. The precipitate is washed and dried and may be mixed with fillers. The alkali metal tannate remains in the shellac product.

An insulating composition is prepared by Barringer ⁸⁶ by dissolving 1 part of shellac in $2\frac{1}{2}$ parts of hot water containing a small amount of ammonia. This is diluted somewhat (to sp. gr. 1.015) and mixed with sodium silicate in the proportion of $1\frac{1}{2}$ parts of the shellac solution to 10 parts of sodium silicate having a specific gravity of 1.46. A filler such as siliceous earth is added. The composition serves as a cement and also may be used for coating and impregnating purposes. Coils impregnated with the solution and baked for 12 hours at a temperature between 100-150° C. show great resistance to higher temperatures and do not blister in the manner exhibited by many resinous compositions.

Fish Meal and Formaldehyde.

A product obtained by treating fish meal or fish guano with acids and precipitating with a large quantity of water or a calculated quantity of alkali is rendered insoluble either by heating to 100-180° C. or by warming with an aldehyde (formaldehyde or furfural) and is then mixed with a fibrous or pulverulent filler. During the stage of rendering the precipitate insoluble it may be mixed with a small quantity of a ketone or phenol or tar oils, etc. Unless filling material is added the resistance to breakage is low.⁸⁷

⁸⁴ J. S. C. I. 1916, 35, 530; German Pat. 290,599, Sept. 22, 1914.

^{84a} German Pat. 314,418, Feb. 14, 1918.

⁸⁵ U. S. Pat. 1,227,465, May 22, 1917.

⁸⁶ U. S. Pat. 1,423,985, July 25, 1922.

⁸⁷ Plauson, German Pat. 352,534, 1920; J. S. C. I. 1922, 41, 722A.

Chapter 23.

Certain Resinous Products Derived from Fatty Oils.

Although fatty oils are largely utilized in the preparation of many plastic mixtures, in nowise do these oils contribute extensively to the actual production of synthetic resins. The present chapter does not embrace the numerous plastic compositions containing fatty oils in mere admixture (usually heat-treated to modify their nature) but describes a few resinous substances or plastic masses obtained by chemical action of an order better serving to bring the products within the confines of the synthetic domain.

Oxidation by Nitric Acid.

A binding material has been prepared by Cadoret¹ from saponifiable oils by oxidation with nitric acid and subsequent saponification. The soap is acidified and the liberated resinoid substance is purified. Cadoret named the product "resinoline."

Chinese Wood or Tung Oil.

Reference has been made in Chapters 15 and 16 to the importance of Chinese wood oil or tung oil in hardened rosin and ester gum varnish compositions. The gelatinization of Chinese wood oil on strongly heating is a change so well known and so frequently described that the phenomenon requires only passing mention. Protracted heating of the gelatinized substance yields a product possessing resinous properties in greater or lesser degree.

Tung Oil and Toluidine.

Lilienfeld² has made resinous compositions by heating Chinese wood oil with toluidine and a condensing agent. A hardening effect may be obtained by treatment with formaldehyde. A product of a resinous nature is obtained by heating one kilo each of ortho toluidine and Chinese wood oil with 150-200 gms. zinc chloride in 60-100 gms. water. The temperature is maintained between 200-300° C. until a satisfactory degree of resinification is reached. When employing formaldehyde the following procedure is recommended. One kilo Chinese

¹J. S. C. I. 1897, 449; Brit. Pat. 12,451, 1896.

²U. S. Pats. 1,037,158, Aug. 27, 1912; 1,090,730, Mar. 17, 1914.

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wood oil is mixed with 1 or 2 kilos of ortho toluidine, the mixture heated to 80° C. and 110 gms. zinc chloride dissolved in an equal weight of water is added. The temperature is gradually raised while agitating the mixture and collecting the excess of toluidine which distills. The temperature of the heating bath is gradually raised to 260-290° C. and is maintained in this neighborhood until the mass becomes hard and resin-like on cooling. The resinified material is kneaded with water to wash out zinc chloride and is heated gradually with 20-200 gms. of aqueous formaldehyde or an equivalent amount of trioxymethylene. A modification of the process involves adding the formaldehyde with the toluidine.

Factis and Amines.

Nuth³ dissolves factis in an amine and obtains a product soluble in volatile hydrocarbons such as benzol or toluol. The factis is made by dissolving a fatty oil in benzol or toluol and treating with sulphur dichloride similarly diluted. When reaction is complete the factis may be separated from the solvent. Factis is made according to proportions given in the following table:

<i>Series</i>	<i>Oil</i>	<i>Sulphur Dichloride</i>
A	Linseed 10 parts	3
B	China wood ⁴ 10 parts	3
C	Poppy 15 parts	4
D	Castor 75 parts	6
E	Cod liver 4 parts	1

Factis prepared as above is dissolved in an amine by heating to 125-140° C. for several hours with stirring. When the factis is in solution a quantity of toluol is added, amine hydrochloride is removed, and the solution obtained may be used as a varnish. The reaction product may be separated and purified by precipitating and washing with alcohol. The following table refers to factis prepared according to proportions given in the preceding table.

³U. S. Pat. 1,159,258, Nov. 2, 1915.

⁴The effect of sulphur on Chinese wood oil is a remarkable one. When most vegetable oils are heated with sulphur, vulcanization takes place with darkening. With wood oil the color, if modified, becomes lighter and even minute amounts of sulphur heated with wood oil have an extraordinary effect on the properties of the oil. retarding or preventing drying.

<i>Factis</i>	<i>Amine</i>
Linseed A 1 part	Aniline 3 parts
Linseed A 1 part	Para chloraniline 1 part
Linseed A 10 parts	Meta nitraniline 7 parts
China wood B 1 part	Para toluidine 1 part
China wood B 1 part	Mono ethyl para toluidine 4 parts
China wood B 1 part	Di methyl aniline 2 parts
Castor oil D 1 part	Aniline 5 parts
Cod liver oil E 1 part	Aniline 4 parts

These products may be hardened by further heating and may be vulcanized with sulphur. Nuth also uses sulphur monochloride in some cases for the preparation of factis.

Chlorinated Oils, Fats and Waxes.

A general procedure for preparing resin substitutes by exhaustive chlorination of various organic substances, proposed by Boehringer⁵ involves dissolving the substance—an oil, fat, wax, or rosin—in carbon tetrachloride and treating the solution with chlorine gas. An increase in temperature accompanies the first stage of chlorination, later a drop in temperature. Chlorination is continued far beyond this point, exposure to actinic light serving to reduce the time required for the reaction. Transparent firm bodies are obtained by the chlorination of linseed and Chinese wood oil. Chlorinated paraffin and ceresin wax show a notable resistance to the action of strong acids.⁶

Chlorinated Tung Oil.

When tung oil is treated with chlorine, until the reaction has somewhat abated and the temperature begins to fall, a body containing about 28 per cent of chlorine is obtained. This product is a thick dark liquid and continuously splits off hydrochloric acid on standing at room temperature.⁷ Further chlorination in carbon tetrachloride solution yields a solid, transparent body.⁸

Hydrogenated Tung Oil.

Hydrogenated tung oil is used by Seigle^{9a} to impregnate asbestos brake shoes or linings; subsequently exposing the material to a temperature at which polymerization of the oil occurs. Tung oil hydrogenated

⁵ C. F. Boehringer & Soehne, German Pats. 256,856, Nov. 19, 1910; 258,156, Dec. 18, 1911; J. S. C. I. 1913, 499 and 613.

⁶ For particulars of the chlorination of waxes see Chap. 5, and of rosin, Chap. 15.

⁷ C. F. Boehringer & Soehne, German Pats. 256,856, Nov. 19, 1910, and 258,156, Dec. 28, 1911.

⁸ Linseed oil behaves in the same manner. Cotton oil is more heavily chlorinated by exposure to light during chlorination.

^{9a} U. S. Pat. 1,436,362, Nov. 21, 1922.

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until its iodine number has fallen to 120-130 with or without the addition of a small percentage of gilsonite is used for impregnation and thereafter the temperature of the impregnated material is raised to 240° C. to effect polymerization.

Baekeland's Tung Oil Process.

Tung oil is heated to 205-210° C. without solidification, mixed with a filler such as wood flour, asbestos or silex and the mixture molded and baked. The molded articles are given a coating of asphalt or phenolic condensation products. Electrical insulators may be made in this manner.⁹

Tung Oil and Metallic Chlorides.

Scobel¹⁰ makes use of the reaction between tung oil and anhydrous chlorides. On grinding anhydrous ferric chloride or its hydrates with tung oil, a solid is produced which is non-coherent, yellow in appearance and which gradually darkens. When the ferric chloride is ground in an indifferent oil such as rosin oil or linseed oil, and then quickly mixed and incorporated with the tung oil a homogeneous mass is formed. If allowed to solidify in molds these products retain the shape of the container. The solidification is accompanied by a perceptible increase of temperature and in volume. The molded articles are very glossy, opaque in bulk and jet black in appearance, translucent in thin sections, however. When first removed from the mold or container, the solid substance is slightly tacky but soon loses this property on exposure to the atmosphere, or when kept at a temperature of about 90-100° C. for a few hours. Prolonged exposure to elevated temperature has a hardening effect on the mass. The outer portions which are in contact with the atmosphere become very much firmer than the interior. With zinc chloride, the solid products are brown to deep red, sometimes they are translucent; aluminum chloride gives a very deep brown to black color.

Rosin and ester gum or other oil-soluble gums can be employed up to 40 per cent by weight of Chinese wood oil used. When quantities in excess of 40 per cent are employed the product is deficient in resiliency, is quite brittle and softens at temperature somewhat above room temperature.

Chinese wood oil fatty acids can be solidified by use of active chlorides in anhydrous solvent, but preferably in conjunction with raw or blown Chinese wood oil. Chinese wood oils that have been partially polymerized by prolonged heating or at very high temperatures are unsuitable because products solidified from these oils will soften and grow sticky at comparatively low temperatures. Chinese wood oil that has been heated above the polymerization point with small amounts of sulphur can be solidified in the usual manner.

When using Chinese wood oil alone, 1 kilo of oil requires 25 cc. 20 per cent solution of ferric chloride in anhydrous acetone, to cause solidification. As

⁹ U. S. Pat. 1,312,993, Aug. 5, 1919, and 1,372,114, Mar. 22, 1921.

¹⁰ U. S. Pat. 1,383,864, July 5, 1921.

much as 150 cc. can be used on that quantity of oil and a firmer product secured. When using Chinese wood oil containing rosin or ester gum somewhat larger amounts of solution or a stronger solution can be employed.

Usually most additions such as rosin, wood flour, cork, fillers and coloring minerals exercise a retarding influence on solidification; and in working formulae it is found desirable to use larger amounts of ferric chloride solution or stronger solutions in such compositions.

A formula suitable for slabs, for tile or flooring, etc., is: 8 kilos Chinese wood oil, 2 kilos rosin, dissolved by warming and ground with $1\frac{1}{4}$ kilos each of infusorial earth, wood or cork flour, oxide of iron (red). A kilo of a solution of ferric chloride in anhydrous acetone is added. This solution is made of equal parts by weight of ferric chloride ($6\text{H}_2\text{O}$) and anhydrous acetone.

Another formula is: 1 kilo Chinese wood oil containing 40 per cent rosin, $\frac{1}{2}$ kilo Chinese wood oil containing 10 per cent ester gum, 50 grams cork meal, 50 grams wood flour, 100 grams Indian red, 200 grams magnesium silicate or other mineral filler. 100 cc. of a solution made as follows: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ 1 kilo, anhydrous acetone $\frac{1}{3}$ kilo, is added.

When operating on pure Chinese wood oil without fillers or additions of any kind, the oil can be made to solidify, with difficulty, however, although accelerated by warming, when less than $12\frac{1}{2}$ cc. of 20 per cent ferric chloride ($6\text{H}_2\text{O}$) in anhydrous acetone per kilo of oil is used. The solid mass is quite translucent and of poor mechanical properties.

25 cc. of this 20 per cent solution solidifies Chinese wood oil quite readily. Using 50 cc. the oil mass is firm, tough and opaque and can be hardened still more by keeping in a warm place for twenty-four hours. Stannic chloride (anhydrous) in cooled anhydrous acetone also produces an active solidifying solution. The pure fuming anhydrous chlorides of tin or antimony cannot be used in this condition for their action on Chinese wood oil is too energetic. Much weaker solutions of these liquid chlorides in an indifferent solvent such as benzene cause clotting or non-uniform solidification.

Polymerized Castor Oil.

The polymerization of castor oil in the presence of metallic oxides giving rise to formation of metallic soaps affords a composition for coating wire which, according to Harris,¹¹ can be solidified in contact with wire by heating to about 300°C . for three minutes or less. Copper, ferric or aluminum oxide, also alkaline earth oxides, are heated with castor oil to $250\text{--}310^\circ\text{C}$. until 5-15 per cent of the castor oil has distilled. The composition while hot is readily soluble in turpentine, pine oil or solvent naphtha. Metallic resinates and fossil resins also may be employed.¹²

Miscellaneous Compositions.

Ferrous linolate, dissolved in a solvent, e.g., turpentine oil or dichlorobenzene, or in drying fatty oils or fatty acids, forms the basis of a paint medium.¹³ The crude saponification products obtained from wool-fat by Lifschutz¹⁴ are treated with solvents in which the unsaponifiable matter dissolves but the soaps are insoluble. The former can then be used for varnishes. Loeschigk¹⁵ utilizes the foots obtained in refining cottonseed oil and similar products consisting of

¹¹ U. S. Pat. 1,240,566, Sept. 18, 1917.

¹² U. S. Pat. 1,240,567, Sept. 18, 1917.

¹³ A.-G. für Anilin-Fabr.; Ger. Pat. 339,574, Nov. 8, 1919; J. S. C. I. 1921, 40, 742A.

¹⁴ German Pat. 345,433, Dec. 1, 1918.

¹⁵ J. S. C. I. 1910, 640; German Pat. 220,582, Sept. 26, 1909.

RESINOUS PRODUCTS DERIVED FROM FATTY OILS 357

soaps, neutral fats, resins, and albuminous substances. This raw material is oxidized in alkaline solution (e.g., by hydrogen peroxide), and then treated with acid, when the fatty matter separates and may be recovered by means of a solvent. The residue is an amorphous, resinous mass.¹⁶

Recovery of Old Varnishes.

Resinous substances are obtained by dissolving old varnish or resin coatings in solutions of sodium or ammonium carbonate or hydroxide, sodium borate, etc., and treating the solution with sodium hypochlorite or free chlorine. The resin solution is precipitated by sulphuric acid or sulphur dioxide. The dried precipitate is used in the preparation of varnishes.¹⁷

¹⁶ The so-called "liquid resins" (German Tallöl or Talloel) or semi-resinous semi-solid substances obtained as by-products in the sulphate and sulphite process of paper pulp manufacture are so objectionable in odor and so contaminated by sulphur compounds and foreign bodies that very little attention has been paid to these raw materials as a source of resin. Possibly they may be used in making greases and in other applications where a better grade of resin is not required. The quality of the best resins obtained from these sources is such that competition with even ordinary rosin is scarcely possible. Much work is needed to recover from "liquid resins" any products of more than nominal value. Note Klemm, *Chem. Z.* 1910, 34, 1353; *J. S. C. I.* 1911, 37. Von Euler states the liquid resin obtained as a by-product in the sulphate pulp process owes its consistency to the presence of a large amount of unsaturated fatty acids, the content often being as high as 50 or 60 per cent (*Arkiv. Kemi. Mineral. Geol.* 1921, 8, 21). When crude talloel is refined by distillation a so-called "talloel pitch" is obtained. Hubscher, *Seifensieder Z.*, 1921, 48, 231.

¹⁷ Littleton, U. S. Pat. 1,308,438, Nov. 29, 1921.

Chapter 24.

Plastic Molding.^{1, 2}

Introduction.

Synthetic resins have found a wide field of utility as binders for molding compositions. This application, which is an art itself, due to the comparatively recent advances in the development of these resins, is demanding more and more attention from manufacturers of electrical instruments and apparatus as well as from the automotive, phonographic and numerous other industries.

The section of the book devoted to plastic molding is intended to familiarize the research chemist and the consumer of molded products with the general properties obtainable, the materials required, the equipment and methods of manufacturing and molding plastic compositions with synthetic resin binders. Methods of testing molded products to determine their properties are also given. To the manufacturer of molding compositions and to the molder this section may be of value in the education of employees and for general reference.

Due to the infinite number of variations in the properties of synthetic resins even of the same type and the different shape and requirements of molded articles, it is not possible to lay down fixed rules for methods of manufacture, fillers required, design of molds or methods, of molding. Each resin, molding composition, and article to be molded presents its own problems and the information available in this volume concerning present methods and products should be helpful in meeting new problems as they arise.

Part 1. Properties.

The plastic molding of a mixture of resinous binder and non-resinous filler, yielding articles which are replacing wood, metal and other materials to a large extent, is the shaping of a plastic composition in a mold, conforming to the shape of the desired piece, by means

¹ Chapters 24, 25, 26 and 27 were prepared in co-operation with Mr. Trevor S. Huxham, in charge of the molding department of the author's experimental synthetic resin laboratory, and the author wishes to express his appreciation of the painstaking study and investigations undertaken by Mr. Huxham in the comparison of the molding properties of many varieties of resins of the most diverse chemical constitution.

² The author desires to acknowledge his indebtedness to the General Bakelite Company, New York, for illustrations of hot molded products appearing in this chapter.

of a comparatively great pressure, with or without heat. Two distinct processes are recognized in molding practice: the "*hot process*" and the "*cold process*." Molding compositions for the hot process normally differ from those of the cold process in that compositions for hot molding, as the name implies, require heat to render them plastic, whereas compositions for cold molding are plastic at room temperature. Synthetic resins have been used to a much greater extent in hot molding than in cold molding, and the following pages, therefore, are devoted more exhaustively to hot molding compositions and methods. In this process, when the material is placed in the mold and subjected to heat

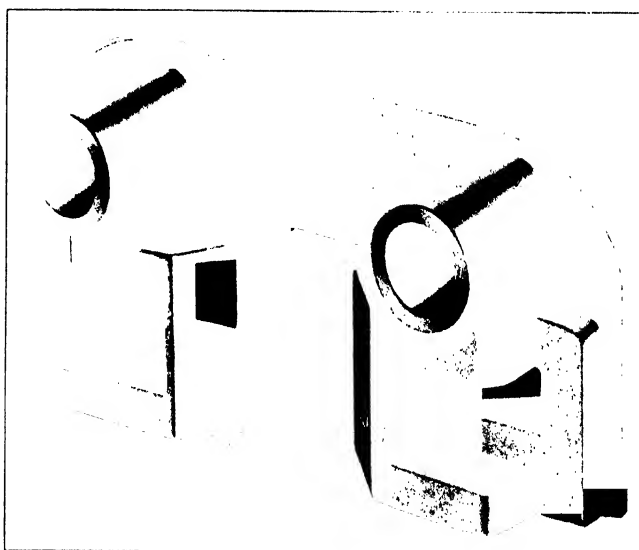


FIG. 13.—Illustrating Irregular Shape.

and pressure, the binder, consisting of a resinous material of some sort, melts and flows together and at the same time forms a thin film on the outer surface of the article. If the resin is of the so-called fusible type the action is merely that fusion renders plastic the whole mass and the shaped article is chilled before taken from the mold so that the impressed form is retained, but the article may again be heated and re-shaped. The thermo-setting type of composition receives the same treatment except that the heat and pressure applied to the mold brings about a reaction which renders the product infusible.

Uses.

It is possible in many cases to substitute molded parts for metal and other materials requiring elaborate machine treatment, with a

saving in cost and improvement of product. One of the principal reasons for this is the time and labor eliminated by reducing the multiplicity of operations, often required to produce an article from metal or some other material, to one operation—molding. Not only may the material be shaped as desired, containing holes, screw threads, figures, letters and designs as shown in Fig. 14, but it may be possessed of a high surface lustre requiring little or no finishing treatment. This is especially true of the hot molded products. Cold molded articles do

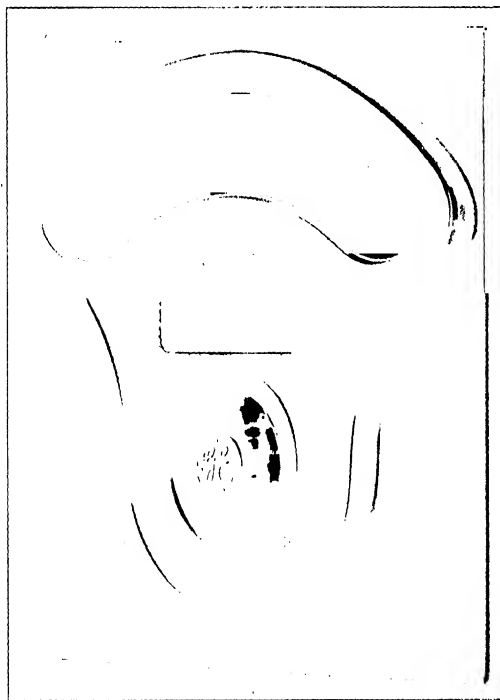


FIG. 14.—Showing Lettering and Embossing.

not have the same smooth homogeneous surface and lustre, as will be evident from an examination of Fig. 16, which is a photograph of a cold molded article. Pieces of metal, rubber or other materials may be embedded in the article at the time of molding, according to the requirements.* Fig. 18 shows a terminal block with so-called “inserts” about which the composition has been molded. At the same time the inserts are insulated so that the block may be employed for electrical purposes.

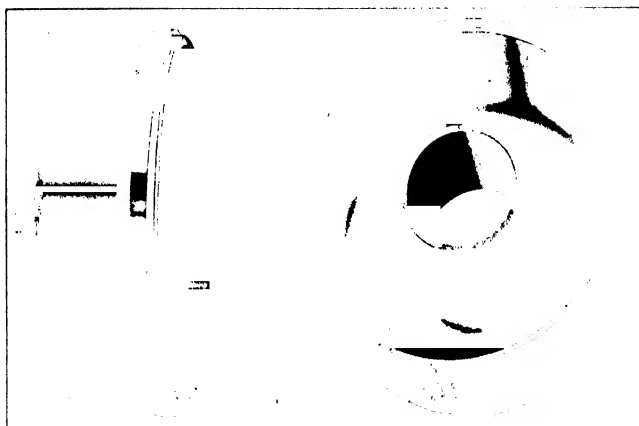


FIG. 15.—Examples of Threading and Thin Wall Molding.

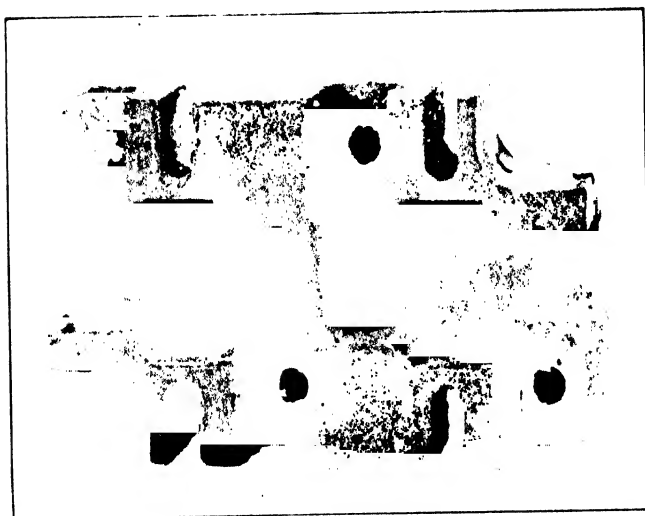


FIG. 16.—Cold Molded Article.

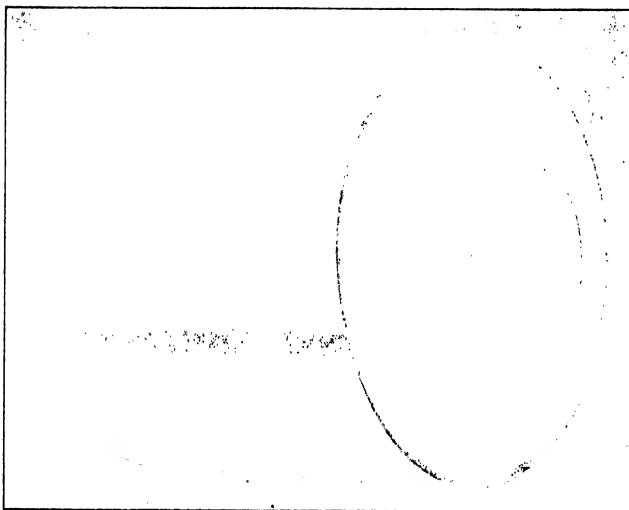


FIG. 17.—Hot Molded Article.

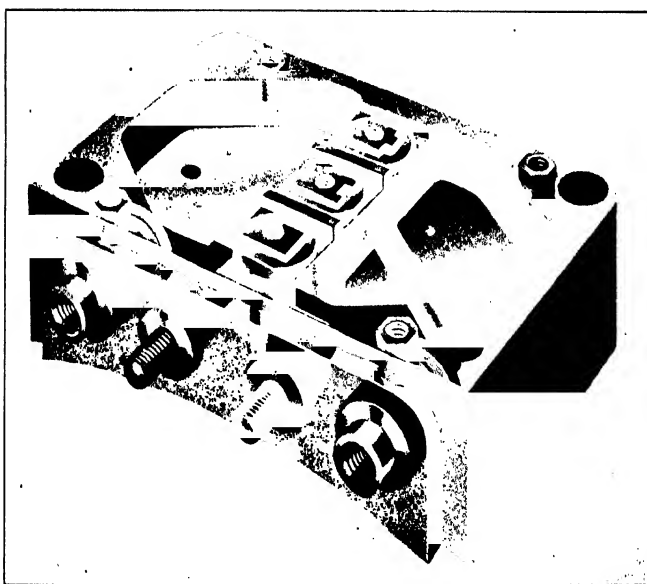


FIG. 18.—Phantom View of Molded Terminal Block Showing Inserts.

Variations in Properties.

The properties of the different molding compositions vary just as the properties of different metals deviate widely and various combinations of properties occur to meet the need of different uses. The cost of molding compositions and molding also varies,—for example infusible cold molded products are lower in both raw material cost and molding cost than the hot molded infusible compositions but the latter possess a better appearance, greater mechanical strength and higher dielectric properties than cold molded compositions. Each product,

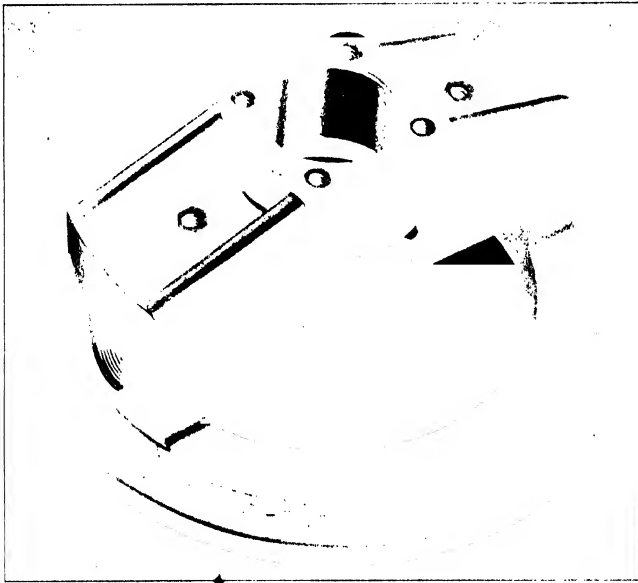


FIG. 19. —End Frame for Electric Drill.

however, has its field. The fusible compositions employed are usually considerably less expensive than those which molding renders infusible and are molded at a lower cost. A fusible composition of shellac and filler for sound records is satisfactory and is used in preference to an infusible product. The particular requirements of the article desired therefore decide the proper molding composition to be used. The properties of molded products of the same make vary sufficiently to offer difficulty in furnishing precise data which will be applicable in *all* cases. For instance, samples from the same composition molded in a highly polished mold and also in a dull finished or poorly polished mold will show different electrical insulating properties. This is due to the fact that a film of moisture and dirt will form on the dull or uneven

surfaced article more readily than on the more highly polished surface and will considerably decrease the surface resistivity. The Bureau of Standards has published a table included in this chapter showing a comparison of the properties of hard rubber, vulcanized fibre, laminate and molded phenol-formaldehyde resinous insulating materials. This appears in the Bureau of Standards Technologic Paper No. 210 (July, 1922).

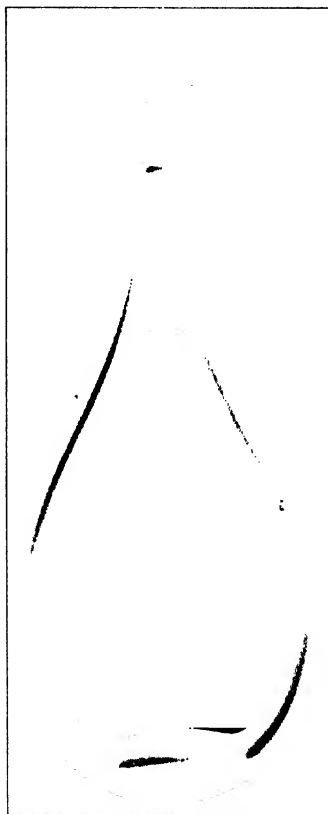


FIG. 20.—Strap-Handle for Street Car.

Most of the hot molded type and are readily recognized by the characteristic smoothness and homogeneous surface, together with a high surface lustre which is permanently retained by high grade product of this type. Figures 13, 14 and 15 illustrate a number of these articles.

Mechanical Strength.

The mechanical strength of molded products is perhaps of primary importance. For instance in the manufacture of commutators for electric motors the segments of a commutator are bound together by

Color.

Molded products are prepared in several colors, black being most widely used with brown nearly as much in demand. Red, green, blue and other colors are also prepared. Lighter colors and white are seldom seen. The white and light-colored phenol-formaldehyde resins, formerly very quickly darkened by light are now produced of ivory color of considerably improved light stability. Ivory, white, and nearly colorless transparent products have been prepared in the author's laboratory by several widely different methods employing hot molding. The various molding compositions, although differing so greatly in electrical and mechanical properties, are more or less similar in their external appearance.

Surface Finish.

Most of the molded articles which are used in places where they will be readily seen are usually

a molded part, and, due to the high centrifugal strain occurring when a motor is operating, considerable strength is needed in the molding composition to keep the segments from flying apart. Figure 21 illustrates sections of commutators which are molded from some of these products. In the manufacture of billiard and bowling balls molding compositions have been used because of their strength, hardness and resiliency. Compositions of the phenol-formaldehyde resin type have proved superior to any other products used for billiard balls with the exception of ivory; although somewhat darker in color than ivory.

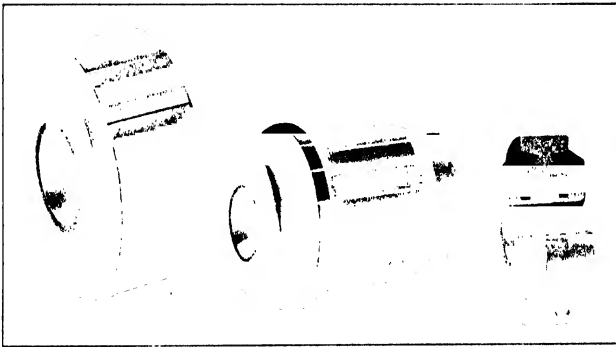


FIG. 21.—Commutators for Motors.

Heat Resistance.

The effect of heat on molding compositions is second in importance only to mechanical strength. Molding compositions which will not withstand a temperature of 100° F. are suitable only for use in moderate climates and even then care must be taken that they are not placed near radiators, in the direct sunlight or near other sources of heat. The great fault of shellac molding compositions is their comparatively low heat resistance. Articles made from shellac molding compositions will warp and be distorted by the sun's rays or even at moderate room temperatures when subjected to some pressure. For instance shellac molded castors for furniture are unsatisfactory because if allowed to stand for a long time in one position the castor will flatten. Molding compositions of the infusible type withstand continuously temperatures up to 150° C. (about 300° F.) and up to 300° C. (about 570° F.) for short periods, provided the articles are not exposed to alternate heat and cold and unusual dampness; as these conditions tend to spoil the surface, at least for electrical insulation purposes. However, some of these infusible compositions have been used in moist places, for example, in valve discs for steam lines and have proved satisfactory for this purpose. When so used the products are usually prepared with a water-resisting inorganic filler, such as asbestos.

Dielectric Properties.

The dielectric properties of molding compositions have been carefully studied by the manufacturers. The Bureau of Standards also has given the subject a very careful investigation. Quantities of composition are being used for high tension work where only the very best insulating materials can be employed. The large majority of uses of molding compositions for electrical insulation necessitates products having only very moderate insulating properties. Not infrequently high tension insulation is used where nothing more than ordinary house lighting current is employed. In some cases, of course, other properties, such as high mechanical strength and resistance to high temperatures, make necessary the use of more expensive products, but in many instances it is possible to use a composition of inferior quality with a saving in material cost and often a great reduction in molding

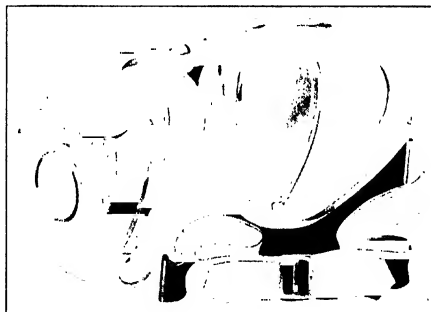


FIG. 22.—Goggles for Industrial Purposes.

cost. The users of molded products have very often failed to study out the exact requirements of their molded articles and are using expensive materials which are not justified.

Other Properties.

A number of uses for molding compositions have been found where the product must be unaffected by weather, chemicals, acid fumes, solvents, etc. Goggles for industrial uses (see Fig. 22) have been molded of chemically inert compositions which are superior to metal-framed goggles because of their low heat conductivity and freedom from rust or corrosion by acid fumes. In a number of cases articles which must resist acid have been prepared with successful results. There is a demand for a molded battery jar which will satisfactorily withstand electrolytic action and diluted sulphuric acid. Phenol-formaldehyde resin compositions have been employed for this purpose with unsatisfactory results. The jar will withstand the diluted sulphuric acid employed but the effect of electrolytic action, which occurs when the

a molded part, and, due to the high centrifugal strain occurring when a motor is operating, considerable strength is needed in the molding composition to keep the segments from flying apart. Figure 21 illustrates sections of commutators which are molded from some of these products. In the manufacture of billiard and bowling balls molding compositions have been used because of their strength, hardness and resiliency. Compositions of the phenol-formaldehyde resin type have proved superior to any other products used for billiard balls with the exception of ivory; although somewhat darker in color than ivory.

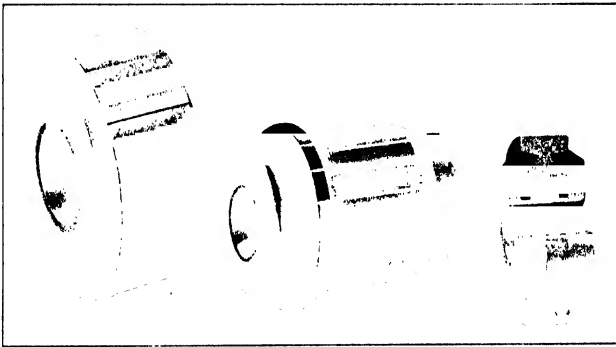


FIG. 21.—Commutators for Motors.

Heat Resistance.

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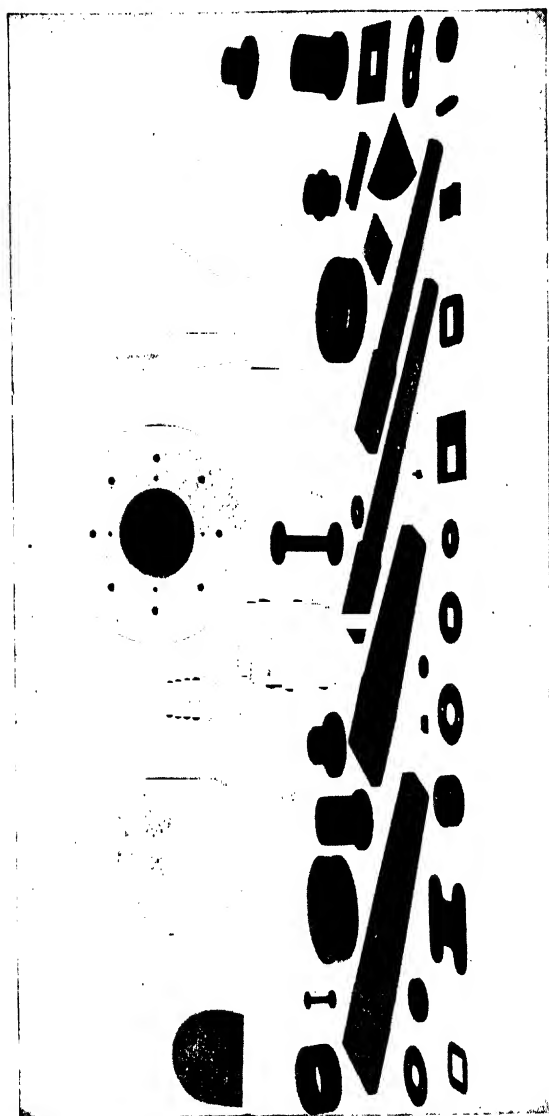


FIG. 24.—Laminated Products. Gears and Punchings.

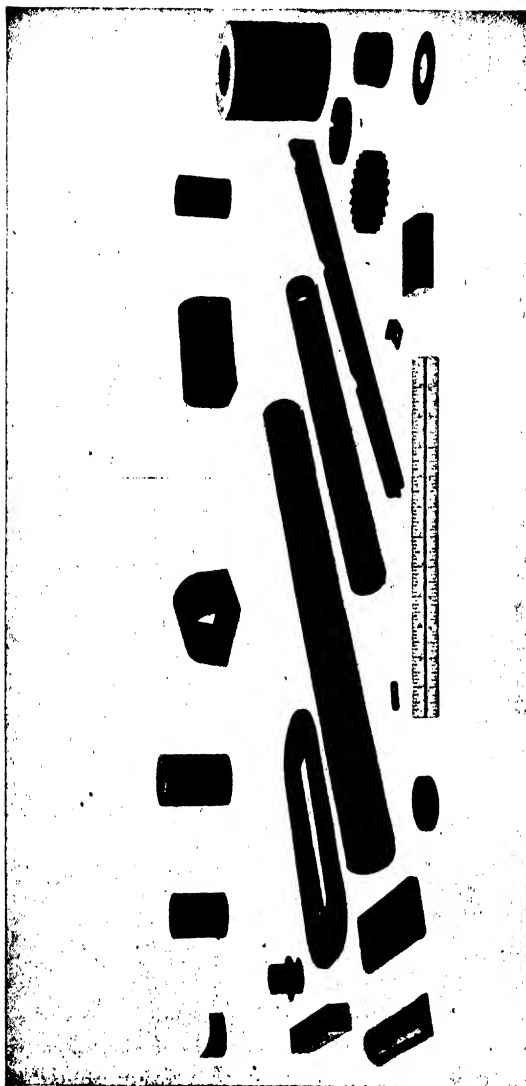


Fig. 25.—Other Laminated Products.



FIG. 26.—Airplane Propeller.

battery is in use, is quite destructive. Most of the above-mentioned compositions may be machined with little difficulty. This is especially true of the infusible type or of those possessing a relatively high softening point. These are readily drilled, planed, filed, sawed, and turned and may be finished to a smooth homogeneous surface which will take a high polish. The fusible compositions possessing a low softening point, such as shellac, will not withstand the heat encountered in machining.

Laminated Products.³

Laminated material consists of superposed sheets of strong paper or canvas impregnated with a resinous substance and subsequently subjected to heat and pressure. These products are made only in sheets, rods, tubes, and a few other special shapes of simple contour, for they cannot be molded in intricate shapes. (See Fig. 23.) The impregnation of the paper or canvas fibre enormously improves the water resistance of these materials. Absorption of water, of course, causes softening of fibre and impregnation with infusible resins, such as those of the phenol-formaldehyde type, overcomes absorption and makes possible its employment for purposes requiring high dielectric and mechanical strength. Laminated products (see Figs. 24 and 25) can be machined, sawed, drilled, punched and polished. Although these materials usually dull cutting tools quickly and require some experience in handling them to obtain good results, the products are used extensively for electrical insulation purposes and have found a wide field in wireless apparatus. Noiseless gears have been produced which, when operated intermeshed with steel gears, exhibit a high degree of endurance. These have recently been adapted for use in automobiles where silent gears are desirable.

A very important use has been found for the filled canvas material in the making of airplane propellers. (See Fig. 26.) An airplane propeller must be unusually strong, tough and light in weight. Propellers which are made of wood are likely to be damaged when an airplane passes through a rain-storm. This is due to the tremendous impact of the propeller against the rain drops. Propellers made from laminated products have withstood this condition more

³ Illustrations (23, 24 and 25) of laminated products were furnished by the Continental Fibre Co., Newark, Delaware.

satisfactorily than wooden ones. Airplanes equipped with machine-guns not infrequently have their propellers damaged by bullets. The guns are supposed to shoot between the blades of the propellers but often the timing device is incorrectly synchronized and wooden blades are splintered by the bullets. Under these conditions it has been found that propellers made from laminated products either are punctured without splitting or else, due to the resiliency of the material, the bullet rebounds.⁴

Comparison of the Properties of Hard Rubber, Vulcanized Fibre, Laminated and Molded Phenolic Insulating Materials.

A comparative summary of the properties of these materials is tabulated below. The table, which was prepared and published by the Bureau of Standards in technologic paper No. 216, is based upon the results of many investigations and the experience of many users and manufacturers. It will be evident that any numerical value or statement given in the following table is an approximation.

Most of the data given in the table are from tests made at the Bureau of Standards. The statements concerning the effects of various tests on the different insulating materials are based on the experience of various members of the Bureau of Standards staff, and upon the experience of the manufacturers of the materials. While it is possible to prepare insulating materials which would give results different from those recorded for any particular property, yet it is believed that this table gives information in a condensed form which will serve to show some of the limitations as well as the possibilities of these products as they are now obtainable commercially.

Part 2. Preparation of Compositions for Hot Molding.

The two general forms of plastic resinous molding compositions, or "compounds," as they often are called in trade parlance, may be designated as the fusible and the infusible type.

Fusible Type.

In the first, or fusible, type a number of the natural resins such as shellac, copals and rosin are employed. The art of molding is constantly undergoing modifications not due entirely to progression but in part to changes in the supplies of available raw materials. Years ago, when shellac was relatively cheap, it was used extensively in molding compositions, being easy to mold and yielding articles of a considerable degree of toughness and possessing a good surface finish. Hence shellac was much prized in the plastic molding field. The outstanding criticism against it was its low softening point. As the industry of plastic molding developed, shellac gradually increased in price and other

⁴The airplane propeller illustrated was prepared from Bakelite micarta, manufactured by the Westinghouse Electric and Manufacturing Company.

Comparison of Properties of Hard Rubber, Vulcanized Fiber, Laminated and Molded Phenolic Insulating Materials*

Properties	Hard Rubber	Vulcanized Fiber	Phenolic Insulating Materials	
			Laminated	Molded
Surface resistivity at 50 per cent relative humidity, difference (ψ) at radio frequencies, degrees	10^{12} to $>10^{15}$	10^{11}	10^{11}
Dielectric constant (K) at radio frequencies	0.5^a	3.0 to b	1.5 to 4.0	1.5 to 4.0
Dielectric strength, volts/mm.	3.0^a	5.0^b	4.5 to 6.0	5.0 to 7.5
Tensile strength, lbs./in. ²	$10\ 000$ to $38\ 000^c, d$	$9\ 000$ to $16\ 000^c, d$	$27\ 000$ to $45\ 000^c, d$	$9\ 000$ to $40\ 000^c, d$
Water absorbed in 24 hours, percentage by weight	$3\ 500$ to $6\ 500$	$9\ 000$ to $20\ 000$	$10\ 000$ to $25\ 000$	$3\ 500$ to $7\ 000$
Density, g/cm ³	0.02	2.6 to 4.5^e	0.2 to 1.0	0.95 to 0.2^g
Thermal expansion (at 20 to 60° C)	1.12 to 1.40^h	1.3 to 1.5	1.3 to 1.4	1.3 to 1.4
Effect of age.....	60 to 80×10^{-6}	27×10^{-3}	20 to 30×10^{-6}	25 to 45×10^{-6}
Heat	Deteriorates slowly, but if properly vulcanized and protected from the light it is not affected	Improves in quality by seasoning ⁱ	Improves ^j	No depreciation in physical or chemical properties; slight increase in hardness ^j See statement for laminated materials ^l
Sunlight	At 65.5° C (150° F) pure hard rubber softens perceptibly; at 100° C (212° F) it is so soft it may be bent easily; at 15.5° C (60° F) it becomes brittle; at 124° C (255° F) it becomes so hard that it may readily be cut with a knife; melts at 205° C (392° F) ^c Discolors and disintegrates after a few months; the sulphur of the hard rubber is oxidized, forming the equivalent of sulphuric acid; this may take up ammonia from the air or may attack the filling materials forming the atomic structure of the surface; the surface resistivity is greatly reduced ^m	Will not melt under any circumstances; not readily inflammable; chars and becomes brittle; active combustion begins at about 343° C (650° F)	Not readily inflammable; will withstand continuously at (300° F); heat tends to complete the reaction and volatile substances are driven off. Hence, when cooled it shrinks considerably and may split; shrinks 6% C ^k increases in weight above 60° C ^k	After two and one-half years some materials show a slight change, such as discoloration or very fine cracks; other materials show no such change ⁿ

Effect of ultra-violet light for 20 hours	Discolor and disintegrates; the action is as pronounced for a few hours' exposure to ultra-violet light as for many months' exposure to bright sunlight. The surface resistivity is greatly reduced. ^m	No data	Appreciable lowering of surface resistivity	Appreciable lowering of surface resistivity ^m
Moist air	Hard-rubber compounds excepting those containing organic substances other than rubber are practically moisture proof.	Absorbs water freely, but without permanent injury, which is retained and becomes soft and flexible and swells; warps and twists upon drying.	Absorbs slight amount of water, reducing dielectric properties.	Absorbs slight amount of water, reducing dielectric properties.
Steam	The only effect is that due to the high temperature.	Same as above, except absorption is more rapid.	Best grades not affected beyond slight absorption of moisture; the steam is impregnated, the high temperature will cause decomposition.	Absorbs a slight amount of moisture; if steam is impregnated, the high temperature will cause decomposition.

^a These values were obtained at frequencies between 250,000 and 75,000 cycles per second (100 to 4,000 meters wave length), there being very little change in the results. The grade of the sample tested is unknown, so values differing somewhat from these might be expected on other samples.

^b Values of ψ and K may be somewhat lower or much higher, depending on amount of moisture present in the fiber.

^c Information obtained from sources other than the Bureau of Standards.

^d Values vary with the thickness of sample, kind of filler, shape of electrodes used, rate of increase of voltage, as well as atmospheric conditions under which tests are made.

^e The Railway Signal Association specifications require an absorption when immersed in water at 70° F for 24 hours, not to exceed 45 per cent by weight for one eighth inch thick, 26 per cent for three-sixteenth inch fiber, and 26 per cent for one-fourth inch fiber.

^f Varies with polish of mold, press pressure, and temperature, length of curing, ratio of resin to filler, kind of filler, and size of sample.

^g The density depends on the amount of sulphur present and increases with the increase in amount of filler. Pure hard rubber ranges from 1.12 to 1.25. A fair commercial quality ranges from 1.23 to 1.40.

^h This means seasoning or aging in a protected place, such as a storage house.

ⁱ These materials are of comparatively recent date, and hence no information has been gained covering very long periods. Theoretically, under certain conditions the materials would tend to continue, which would age and improve the material. One manufacturer claims a slight improvement in dielectric properties and a marked improvement in machining qualities when the aging takes place under ordinary atmospheric and temperature conditions. If the aging takes place in a moist atmosphere, the dielectric properties are subject to deterioration.

^j See pages 580 to 583 and 187, Tech. Papers No. 216, Bureau of Standards.

^k When subjected to temperatures above 60° C (140° F) some of the volatile matter is driven off, resulting in the shrinking and loss in weight of the material. This can be carried out many times with the same result, in any way. It seems altogether probable that a point would be reached that they are very erratic in behavior and do not expand uniformly.

^l After all volatile matters are removed, the material is subjected to a moderate temperature and subsequent cooling would not result in further shrinkage. This has not been proved experimentally. High temperature will produce decomposition. Further information regarding these tests will be found in Scientific Paper of the Bureau of Standards No. 352. (See also pages 580 to 583 and 187, Tech. Papers No. 216.)

^m A further discussion of the tests at the Bureau of Standards may be found in Scientific Paper of the Bureau of Standards, No. 234.

ⁿ See effect of ultra-violet light.

^o See discussion on pages 599 and 600 of Tech. Papers, No. 216, Bureau of Standards.

^p This table is reprinted from Technologic Papers of the Bureau of Standards, No. 216.

Comparison of Properties of Hard Rubber, Vulcanized Fiber, Laminated and Molded Phenolic Insulating Materials—
Continued

Properties	Hard Rubber	Vulcanized Fiber	Phenolic Insulating Materials	
			Laminated	Molded
Solvents:				
Acetone	Attacks, dissolving oils and free sulphur ^c	No permanent effect ^e	No effect ^{e,p}	No effect ^{e,p}
Alcohol	Attacks to a slight degree ^edo. ^edo. ^{e,p}	Do. ^{e,p}
Ammonia	No effect ^edo. ^e	Strong solutions may cause material to swell ^c	No effect other than slight absorption of moisture ^c
Aniline	Softens it at ordinary temperature ^e	Not known	Probably no effect ^e	Probably no effect ^e
Benzoldo. ^e	No permanent effect ^edo. ^{e,p}	Do. ^{e,p}
Carbon bisulphide	Dissolves small amount of hard rubber and any free sulphur ^cdo. ^edo. ^{e,p}	Do. ^{e,p}
Etherdo. ^e	No permanent effect ^e	No effect ^e	Do. ^{e,p}
Naphtha	Softens and swells to slight extent ^e	No permanent effect ^e	Probably no effect ^e	Probably no effect ^{e,p}
Oil of turpentine	Dissolves in boiling oil ^cdo. ^edo. ^e	Do. ^{e,p}
Oil:				
Mineral	Slight softening ^e	Slight absorption ^e	Practically impervious ^e	Practically impervious ^e
Organic	Unaffected ^edo. ^edo. ^e	Do. ^e
Effect of weak acidsdo	Swells due to absorbed water; may be attacked after some time ^e	Practically unaffected except for absorption of water ^q	Practically unaffected ^r
Weak caustic alkalisdodo. ^e	Does not successfully resist the action of alkali unless very dilute	Does not successfully resist the action of alkali unless very dilute
Stronger acids (HNO ₃ , HCl, H ₂ SO ₄)	Not attacked by concentrated hydrochloric, hydrofluoric, acetic acids; not attacked by sulphuric acid; attacked by nitric acid of less than 1.12 specific gravity ^e	Cellulose fiber attacked soon decomposes	Decomposes; rapidity depends on specific gravity and temperature of acid	Decomposes; rapidity depends on specific gravity and temperature of acid
Stronger caustic alkalis	No effect.....do	Binder and filler decompose ^r	Completely destroy; speed of the reaction depends on the strength of the solution
Ozone	Oxidizes and soon ruins it for electrical purposes	No effect ^e	Not known.....	Not known

Metallic inserts.....do.	No effect.....	No effect
Rapidly deteriorated by contact with iron or copper, the metals themselves being corroded; the inserts should be sealed with tin, paper, unvulcanized rubber, or other mutually protecting medium	Admits of a fine finish; may be sawed, punched, drilled, stamped, knurled, bossed, turned, planed, bent, tapped; tough, resists shock; can not be molded	Admits of a good polish; can be sawed, punched, drilled, knurled, embossed, milled, tapered, either with or against the grain, though not as easily as hard rubber and vulcanized fiber; tough, resists shock; can not be molded	Admits of a fine lasting finish in same manner; can be sawed with difficulty; can be molded accurately to size; quite brittle
Machining qualities.....	Admits of a high polish; machines less accurately than would be expected; the grade the more readily it is machined; quality may be judged roughly by color and texture, toughness, color, and grain of a shaving; has tendency to warp; can be molded to any desired size	Admits of a good polish; can be sawed, punched, drilled, knurled, embossed, milled, tapered, either with or against the grain, though not as easily as hard rubber and vulcanized fiber; tough, resists shock; can not be molded	Admits of a fine lasting finish in same manner; can be sawed with difficulty; can be molded accurately to size; quite brittle
Cost	About \$2 per pound in sheet form	About \$1 per pound.....	Cost varies with complexity of steel molds

e Information obtained from sources other than the Bureau of Standards.

P Strong solvents affect the phenolic binder of the material to a limited extent unless the chemical reaction has been carried to the point where it is in the insoluble state. This condition would render the sheet material too brittle for general use. When water is present, the material will absorb it in a very large amount.

and attack the edge of a sample soon after it comes in contact with the sample. In general weak acids will mar the surface and

* See page 608, Tech. Paper No. 216, Bureau of Standards.

* The action differs for various materials and grades. Some materials resist the action of a 30 per cent solution of H_2SO_4 for several months and will withstand hydrochloric acid without any visible sign of attack. On the other hand, some materials are attacked by this class of acids at once and will form a protective coating. This is the case with the sample as far as further electrical use is concerned, but on removing the sample from the acid and cutting it open it is found that the acid has not penetrated more than one-sixteenth inch after several months' exposure to the acid.

† Thin sheets can be pressed to simple shapes when warm.

resins were added to shellac to adulterate or extend it for molding purposes. Both rosin and hardened rosin (see Chapter 15) were used for the purpose, likewise various other resins somewhat more costly than rosin but less costly than shellac. Finally shellac has become displaced to a considerable extent by mixtures of cheaper resins and asphaltic substances. The latter alone are not very satisfactory, requiring the presence of certain resins to produce a properly flowing mixture yielding an article having a glossy finish. The production of such compositions will be discussed later in this chapter.

Infusible Type.

The infusible or thermo-setting type of composition includes a number of binding compositions, but probably the best known at the present time is that represented by the phenol-formaldehyde resins. A great variety of products of an infusible character are made by cold molding and subsequent baking, which heat treatment confers infusibility or a high degree of resistance to heat upon the baked article. Such products, however, are not classed with the thermo-setting type. The latter embrace more particularly those which are capable of hardening in the mold on exposure for only a few minutes to the heat of the press. The description of the manufacture of these phenol-formaldehyde resins and incorporation with various fillers employed has been furnished in Chapter 7. The methods, however, of incorporating fillers with resins are substantially similar for all resins and the procedures described are, therefore, adaptable to practically any synthetic resin.

The molding compositions discussed in the present chapter ordinarily are prepared in two forms—in sheets, or in powdered or granulated condition. These compositions consist of a resinous binder which is the controlling or vital part, incorporated with powdered or fibrous fillers, or mixtures of both classes of fillers.

Binders.

The binder for any molding composition used in the hot process should have a relatively sharp melting point and be fairly liquid at the molding temperature. A resin that softens somewhat but does not flow readily is not usually employed unless the addition of a small quantity of a flux, for example a solvent of high boiling point, will lend this property to the binder. A binder which is freely flowing at the molding temperature yields not only a sharp impression but also better covers any fibrous material present as a filler. The appearance and saleability of the article, therefore, may depend to a very considerable extent on this property. For use in fusible sheeted compositions this quality is important as the product when warmed should be capable of assuming a plasticity similar to putty so that it may be easily worked with the fingers. On the other hand the fluidity of the binder at the molding temperature should not be so extreme that it will be forced out of the filler and exude from the mold. The binder should flow

only freely enough to secure the proper sharp impression while still possessing a degree of viscosity sufficient to retain it uniformly mixed with the filler. The odor of the binder is not an important consideration but is one, however, which should not be entirely overlooked. The heat of the press enhances the evolution of odor from the material and if the binder is made from a synthetic resin having what the molder chooses to term a "chemical smell" other binders of more agreeable odor will be used in preference if readily available. At room temperature the binder should not be tacky but should present a smooth glossy appearance. At the molding temperature the binder must not liberate any material amount of gases or undergo any degree of decomposition which would cause internal pressure in the mold and staining or sticking. Aside from the properties mentioned, the binder should possess qualities making it of value to the molding composition such as hardness, toughness, appropriate dielectric properties, mechanical strength, resistance to water and chemical reagents. Should it possess rapid hardening or thermo-setting properties enabling molded articles to be quickly made by hot pressing without the necessity of cooling in the mold the composition will have a wider range of utility than fusible non-hardening products. Of course no composition is ideal in every respect and the investigator working in this field can see many opportunities for research which should be productive of results of commercial value. Weaknesses in binders often can be remedied at least to some extent by the employment of proper fillers or the addition of other substances to the composition. Improvements are often made by mixing binders of different properties.

For cheap molded articles such as electrical fittings, push buttons, knobs, handles and the like, black in color and not required to be heat resistant, mixtures of hard native asphalts, asphaltites or wurtzilite asphalt and the like admixed with a resin such as hardened rosin make fairly useful binders. The asphalts and asphaltites used should have a fusing point not lower than 88° C. (190° F.) as the article should have a softening point sufficiently high in order not to be affected by the heat of the sun or temperatures somewhat above ordinary room temperature. As the molded article is frequently subjected to rough usage it, of course, should possess a tensile strength and toughness commensurate with the purpose for which it is to be used. The asphaltic material should exhibit a penetration at 77° F. (25° C.) not exceeding 5 by the consistometer and a tensile strength at the same temperature of not less than 10.⁶ In a sense the employment of asphaltic materials and pitches is for the purpose of cheapening or extending the resinous binder and a number of resins produce tougher and better products when used as the sole binder than when compounded with asphalts. In molding phonograph disc records shellac is by far the most desirable binder and is used in enormous quantities for the purpose. Methods of molding compositions containing this resin have been systematized

⁶ Determinations to be carried out according to Abraham, *Asphalts and Allied Substances*, New York, 1920, 498 and 505.

and standardized to such a degree that no composition containing essentially a natural or synthetic resin other than shellac has been able to make any great headway in phonograph record production. It is true that phenol-formaldehyde resins have been employed with success but only to a limited extent. The erosive action of the needle-point of the phonograph calls for an extremely tough binder and hardened rosin, rosin esters or the copals do not possess the toughness requisite to resist this erosive force. On the other hand, hardened rosin, rosin esters, congo and manila copal and cumaron resin may be employed in the production of knobs and other articles which do not require high mechanical strength. The harder varieties of resins obtained by the action of sulphur chloride on phenol described in Chapter 19 also may be used as binders. The brittleness of cumaron resin has been modified to some extent by the addition of a few per cent of linseed oil. Of course the oil reduces the softening point. In the field of synthetic resins those of the fusible type have not as yet displaced to any large extent the natural resins and mixtures of these with asphalts and asphaltites. The molding trade is still awaiting a cheap synthetic product having the hardness and toughness of shellac but possessing a somewhat higher softening point.

Fillers.

General.

The value of fillers in molding compositions depends upon several factors. In the first place, fillers are cheap while resinous binders in most cases are comparatively expensive, so it is advantageous to use as much and as cheap a filler as possible so long as the properties of the resulting composition are benefited. Resins when pressed into irregular shapes develop, on cooling and especially when a reaction has occurred, tremendous internal stresses due to shrinkage and these are relieved only by the formation of cracks throughout the piece. Fillers play an important part in minimizing shrinkage and in reducing the stresses to a large extent. The improvement of other properties depends upon the nature of the binder, and the kind, quality and quantity of filler or fillers employed. For example, mica, in conjunction with other mineral fillers such as gypsum, is satisfactorily used with shellac or phenol sulphur chloride resins, but mica may not be employed so advantageously with phenol-formaldehyde resins, because the latter do not "wet" or cover the particles, and the strength expected of this type of resin in the infusible form does not obtain. Due to the density of mica and gypsum the percentage of these fillers may often reach 70 to 90 per cent of the composition with a proportional increase in density of the molded article. The use of 70 per cent mineral filler with shellac yields a mechanically strong composition due to the inherent toughness and strength of shellac. Rosin with the same kind and proportion of filler would be very weak. A composition from rosin and 50 to 60 per cent

wood flour, while undoubtedly a poor product from the standpoint of heat resistance, odor, etc., would undoubtedly be considerably stronger mechanically. Thus the choice of fillers depends mainly upon the properties desired of the finished product and the nature of the binder.

Fibrous Fillers.

Wood Flour.

Wood flour or cellulose fibre is perhaps the most universally used of all fillers in molding compositions of the infusible type. The reason is that wood flour, although fairly bulky, is usually advantageous because the resin not only coats but impregnates the fibres, thereby giving additional strength and homogeneity to the molded product. Molded articles prepared from this material are relatively light in weight and possess a high dielectric strength. This filler is made in many grades and is sometimes difficult to secure of a suitable quality for molding compositions.

One of the principal objections to wood flour filler is its voluminous character. The majority of wood flours are too bulky and it is important to choose a grade which is low in bulk. A crude but simple method of testing is to take, say, 20 grams of the sample, place it in a graduated cylinder and tap it on a table until the volume remains constant. The bulk should be less than 80 cc.

and preferably about 65 cc. or less. The bulk expressed as $\frac{\text{cubic centimeters}}{\text{grams}}$ =

$$\frac{65}{20} = 3.25.$$

Upon examination under a microscope the cellulose fibres should appear to be fairly uniform in size and free from particles of foreign matter.

About 80 per cent of the wood flour used for molding compositions should pass an 80 mesh screen. The moisture content as determined by loss in weight on heating at 105° C. for 24 hours preferably should not be over 5 or 6 per cent. The wood flour should not contain metallic or abrasive matter which would injure the mold. The color is not always important; although for light colored products or when no coloring matter is employed in the composition this factor enters into the choice of the filler.

Asbestos.

Asbestos as a filler, although yielding a product fairly low in tensile strength, is resistant to shock due to the long fibres which it is possible to employ and at the same time the product withstands a higher temperature without carbonizing than would be the case if wood flour were employed. Asbestos fibre being impermeable cannot be impregnated with the resin and the coating obtained is insufficient to produce a molded product having as good an appearance as one derived by the use of wood flour. Asbestos filled compositions have many limitations in molding. The asbestos mixtures will not flow as wood flour compositions will. The uncoated fibres stick to the mold and the products have not the same smooth surface which wood flour products exhibit.

Asbestos is marketed in many grades and forms. It possesses little or no tensile strength but is flexible and silky and can be obtained perfectly white. It is used as a powder or "flour" and also in long-fibred form. Articles having a good appearance can be prepared using asbestos flour but these are weaker mechanically than when the longer fibres are employed.

Cotton Flock and Cotton Linters.

Cotton flock and linters are used in proportions ranging from 2 to 5 per cent of the entire mix to enhance the shock-resisting properties of compositions not requiring extreme resistance to heat. They are very commonly used in fusible

and standardized to such a degree that no composition containing essentially a natural or synthetic resin other than shellac has been able to make any great headway in phonograph record production. It is true that phenol-formaldehyde resins have been employed with success but only to a limited extent. The erosive action of the needle-point of the phonograph calls for an extremely tough binder and hardened rosin, rosin esters or the copals do not possess the toughness requisite to resist this erosive force. On the other hand, hardened rosin, rosin esters, congo and manila copal and cumaron resin may be employed in the production of knobs and other articles which do not require high mechanical strength. The harder varieties of resins obtained by the action of sulphur chloride on phenol described in Chapter 19 also may be used as binders. The brittleness of cumaron resin has been modified to some extent by the addition of a few per cent of linseed oil. Of course the oil reduces the softening point. In the field of synthetic resins those of the fusible type have not as yet displaced to any large extent the natural resins and mixtures of these with asphalts and asphaltites. The molding trade is still awaiting a cheap synthetic product having the hardness and toughness of shellac but possessing a somewhat higher softening point.

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Methods of Mixing.

Undoubtedly the most commonly used method of mixing molding compositions is by the "roll method." This method of mixing is well-known in the rubber trade, having been used for years with apparently very little change. By this procedure the resin is first thrown on two revolving steel rolls which are in a horizontal plane and turning towards each other at different rates of speed. These rolls are cored for heating by steam and cooling by water and the space between the rolls is adjustable by means of screws. Fig. 27 illustrates

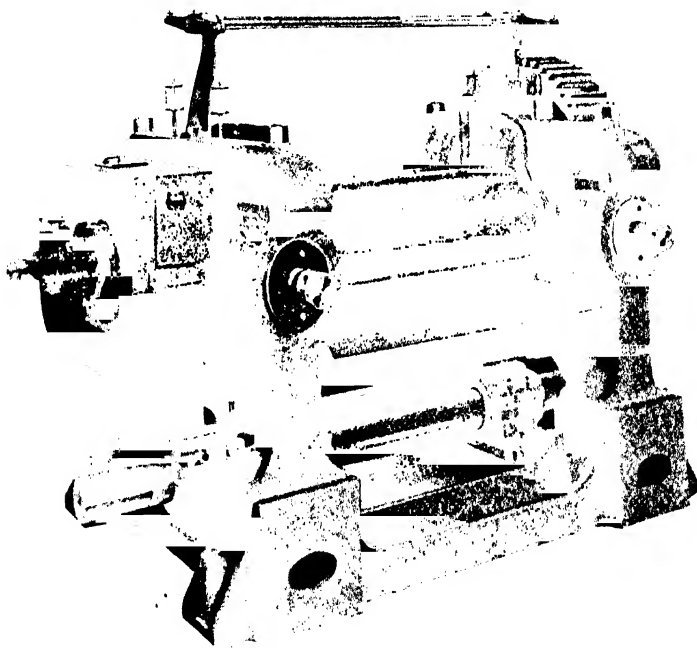


FIG. 27.—Mixing Rolls for Plastics.

a typical set of mixing rolls.⁶ (Occasionally the operator may vary the heating of these rolls. For instance, he may run one roll hot and the other cold or may run both hot, followed by cooling when the mixing process is nearly finished. The regulation of the heating and cooling is determined only by experiment.) After the resin has been melted on the rolls, coloring matter, lubricants and other constituents are added and finally the fillers are thoroughly mixed in. It is usually necessary to start the mixing process with only a small clearance between the rolls and as the filler is added the rolls are

⁶ This illustration, Fig. 27, was furnished through the courtesy of the Vaughn Machinery Co., Cuyahoga Falls, Ohio.

moved farther apart. To facilitate proper mixing and to avoid the effect on the composition of direct contact with the heated surfaces for a prolonged period, stripping knives are usually employed. These may be attached to the rolls and operated by means of a lever or may be entirely separate from the rolls, in which case a rod is fastened on the frame and parallel to the rolls to be used as a fulcrum for the stripping knives. By means of these knives the composition is scraped

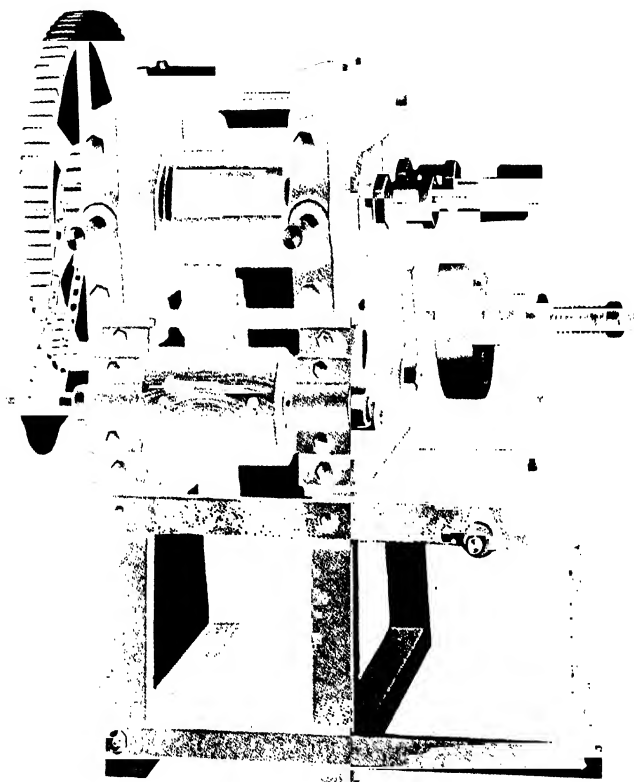


FIG. 28.—Blanketing Rolls for "Sheet-Stock."

off the rolls and is immediately thrown on again until an uniformly mixed mass is obtained. Finally by means of these stripping knives the mix is scraped off the rolls and passed through "blanketing" or sheeting rolls⁷ (see Fig. 28) which are water-cooled and produce a sheet of the composition about one-quarter inch in thickness, of a definite width and length. This sheet by means of fixed blades

⁷ This illustration, Fig. 28, was furnished through the courtesy of the Burroughs Company, Newark, N. J.

on the rolls is cut into standard size lengths and is then ready for molding.^{7a} Instead of sheeting the composition, sometimes the mixture is allowed to cool and is ground to a powder or crushed into coarse fragments in which form it is also used for molding. The use of this method has several advantages. It has been found that a very thorough coating and impregnation of the filler can be obtained which in the opinion of many is superior to any of the more recently developed methods of mixing. The method also has the advantage that drying of the mixture prior to grinding is not required, thus



FIG. 29.—Mixing room showing differential mixing rolls in the rear. On the right are situated blanketing rolls equipped with belt conveyor to remove the sheet stock as formed. On the left is an extra set of blanketing rolls.

avoiding solvent losses, in contrast to other processes where impregnation and coating are effected by means of a solution of the resin in volatile solvents.

Masticators. Safety Devices.

A modification of the roll method has been used to some extent in recent years. The resin and filler are incorporated by means of a heated masticator or mixer. The receptacle of this type of mixer is a steam-jacketed trough and in some cases the blades of the mixer

^{7a} Fig. 29 was provided through the courtesy of Mr. Frank H. Shaw, Shaw Insulator Company, Irvington, N. J.

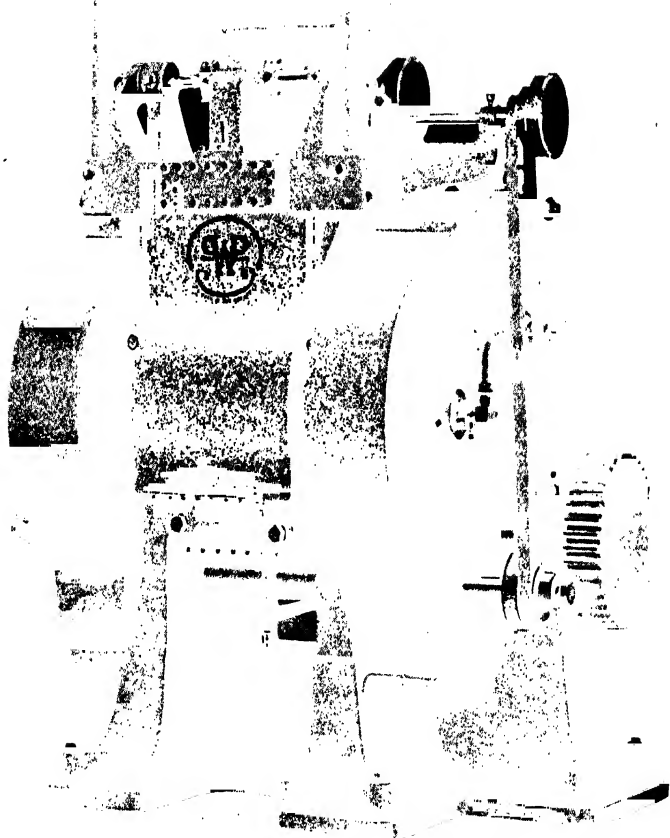


FIG. 30.—Masticator in Operating Position.

are cored to permit circulation of steam or some other heating medium through them. Figs. 30 and 31 illustrate such a masticator or mixer.⁸ These mixers usually have two blades which are made in several shapes according to the nature of the material to be mixed.

⁸ Illustrations 30, 31 and 32 were furnished through the courtesy of Joseph Baker Sons & Perkins Company, agents for the Werner & Pfleiderer Company.

The advantage of the masticator method of mixing is that the element of danger incurred in the use of rolls is practically eliminated due to the fact that the blades are so far removed from the hands of the operator that accidental contact is extremely improbable. This is not the case with rolls as there is very little possibility of guarding the operator and many an accident has occurred by the operator having his hand caught between these rolls. A safety device is

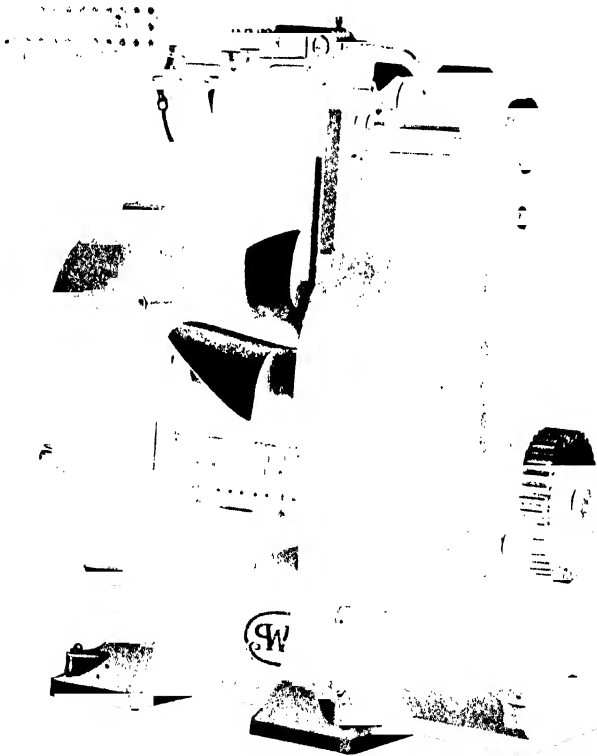


FIG. 31.—Masticator in Discharging Position, Showing Side Discharge Door Open.

now usually installed on the latter, consisting of a rod over the middle of the rolls which actuates a cut-out switch for the driving motor and applies a brake to the rolls. The roll illustrated in Fig. 27 is equipped with such a safety device.

Lack of Uniformity.

It will be seen that the methods described above involve a more or less high temperature to effect mixing. When the thermo-setting compositions are prepared by these methods great care must be ex-

exercised to prevent the reaction proceeding to an extent beyond control. Skilled operators are therefore needed when these methods of mixing are used and even then the production of thermo-setting molding compositions which are uniform from batch to batch in respect to the progress of the reaction is at best a difficult matter.

The Varnish Method.

The varnish method is in common use and consists in mixing a solution of the resin and other soluble constituents in a volatile solvent with the filler and other insoluble constituents in a mixer

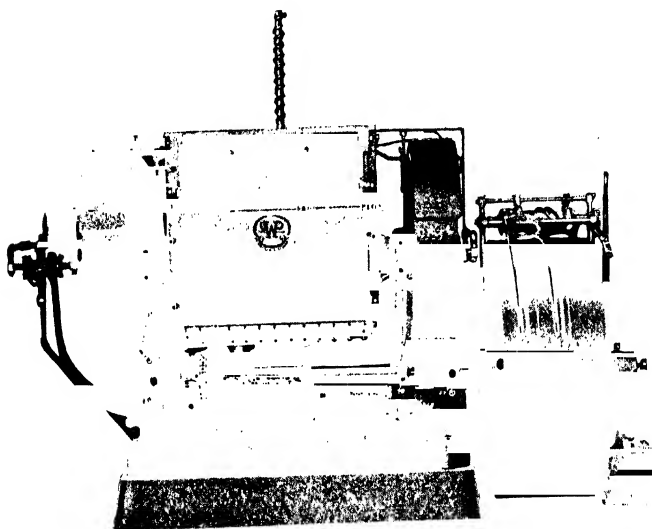


FIG. 32.—Mixing and Kneading Machine. This Type Discharges by Tilting.

of the type shown in Fig. 32. This is somewhat similar to the masticator. The mixer, however, is built lighter and the blades and jacket are seldom heated. Mixing is effected by the blades which rotate at different speeds and are periodically reversed. The machine is automatically tilted for discharge. By this method a solution which usually contains about 50 per cent resin is thoroughly soaked up by the filler and the danger of the reaction proceeding too far is entirely eliminated during the mixing. The product is then dried. In the case of the fusible compositions an ordinary air dryer is satisfactory but thermo-setting compositions nearly always require vacuum drying. This is accomplished in either shelf or rotary drum dryers and carried out in the same manner as described in the manufacture of phenol-formaldehyde resin molding compositions in Chapter 9. Following the drying *in vacuo* or in air the product ordinarily is ground to a powder which constitutes the finished composition. In

some cases, the ground material is placed on rolls of the type already described for mixing, heated to a temperature sufficient to render plastic and after removal from the mixing rolls is immediately passed through sheeting rolls to obtain a sheet composition.

Ball Mill Method.

Compositions containing fillers such as asbestos which cannot be impregnated are sometimes mixed in ball mills. By this method the resinous binder and certain other constituents such as lubricant, flux or plasticizing agent, dyes, etc., are first finely ground together and then further ground with the filler. Occasionally the filler must be ground with a lubricant in which case it is often advisable to do this as a separate operation before combining with the binder. This method of mixing is satisfactory for some purposes but has not a very wide range of use due to the other and superior methods of mixing which have been described.

Preparation of Laminated Materials.

Sheet fibre, paper or canvas are impregnated with a solution of resin, subsequently dried and subjected to heat under heavy pressure, to form sheets, tubes, rods and other simple shapes consisting of layers of the impregnated material. The impregnation is usually effected by passing the paper or canvas through rolls coated with the desired quantity of the resin solution. This is accomplished in a manner similar to the customary method used for coating paper. The coated material is then passed over heated rolls which evaporate the solvent and yield a thoroughly impregnated dry sheet. This is cut into suitable lengths and hot pressed as described in Chapter 25, or marketed in the uncured condition in which form it is suitable for pressing as desired by the consumer.

The resin content of these products range from 30 to 60 per cent. Materials of pre-eminent electrical insulating properties usually contain a high percentage of resin while those requiring better mechanical properties have a content of resin lower than 40 per cent.

The principal problems involved in preparing products of this type are the making of a laminated sheet which will not separate along the laminations, the reduction of water absorption to a minimum, and the production of a hot pressed and cured sheet which will not warp. By the employment of a resin possessing toughness and good cohering properties it is usually possible to prevent splitting along the laminations. The use of a water-resisting resin and thorough impregnation yielding products containing 50 per cent or more of resin minimizes the water absorption. Warping is a defect of considerable importance in these products and presents a problem not yet completely overcome, particularly in thin sheets. This is due mainly to uneven shrinkage caused by stresses set up in the pressing opera-

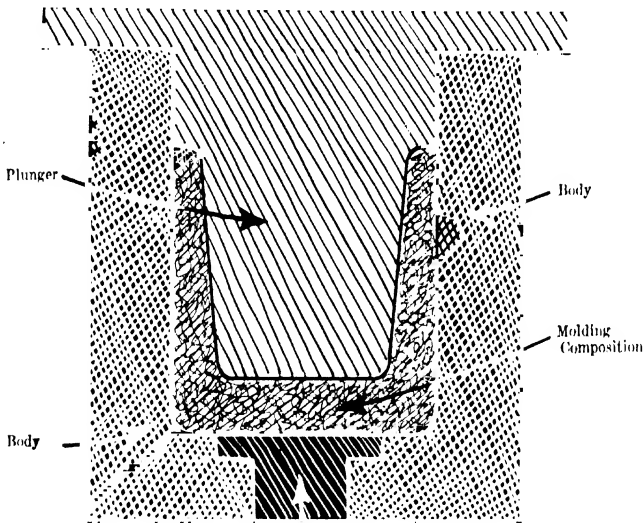
tion. Warping has been overcome to a large extent by "annealing" the pressed sheet. This is effected by subjecting the material to a temperature of 170 to 200° C. (347 to 392° F.) for a short period and subsequently cooling. By repeating this operation two or three times the tendency to warp is markedly reduced.

Chapter 25.

Molds and Molding Equipment.¹

General Construction.

In the matter of design of articles to be molded it is essential to the interests of both the molder and the buyer of the molded article that the designers of the mold and article co-operate. It is only through such co-operation that efficient molding, satisfactory output and low



Ejector or "Knock-out"

FIG. 33.--Cross-Section of Mold, Showing Body, Plunger, Ejector and Composition.

cost for molded articles may be expected. The factors considered in designing a mold are many. When the molder knows the output he must obtain from his molds he can then judge the most economical

¹The author desires to acknowledge his indebtedness to Mr. Charles F. Burroughs and Mr. Walter E. Rahm of the Burroughs Company, Newark, N. J., for data on molding methods and illustrations of molds and presses.

material for the construction of the mold, e.g., soft or hard steel, bronze, etc., the number of cavities per mold and the type of mold most suitable for the work. Fig. 33 shows a cross-section and the principal parts of a mold. In this illustration it will be seen that the mold consists of a body portion or receptable shaping the outer surface of the molded article, a plunger which transmits the pressure causing the material to flow and take the shape of the mold, and a "knock-out" or ejector to facilitate the removal of the molded article. Fig. 34 is a photograph of an assembled mold used for making automobile distributor heads. Fig. 35 shows this same mold in its various

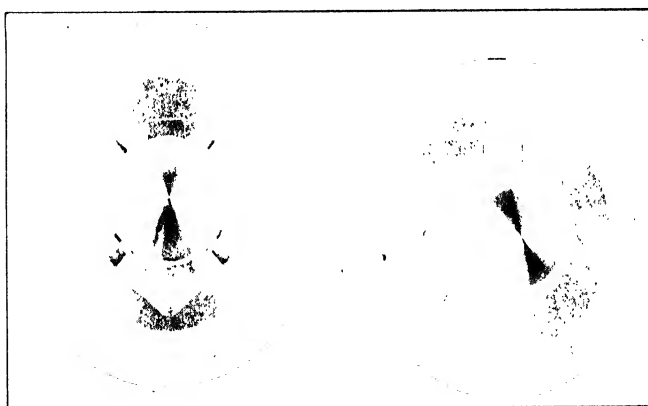


FIG. 34.—Assembled Mold.

parts together with the inserts which are incorporated with the molding composition to form the molded article. In the upper right-hand corner of Fig. 35 will be found the finished article and to the left the inserts. This type of mold is known as a single impression or single cavity positive mold. In many cases, however, molds are made with several cavities. Fig. 36 shows a mold of this type which is mounted in a semi-automatic press. This mold is heated directly by means of high pressure steam which is circulated through cores in the mold itself. The mold illustrated is designed to make toothbrush handles and at the far end of the cavities the ends of small knock-out pins appear which automatically protrude when the press is opened and serve to eject the finished molded articles.

Types of Molds.

There are in general two types of molds, the "flash" or "open" mold and the "positive" or "closed" mold. In the flash mold the top rests upon the body of the mold whereas in the positive mold the top or plunger sets within the body of the mold. Fig. 37, A and B, illustrate the flash and positive molds. Fig. 36 illustrates a flash mold

and it will be seen that around the cavities in this mold an overflow channel has been cut to take care of excess material or "flash." Fig. 38 shows two flash molds for making the ends of player-piano rolls. This type is also a direct heated mold for a semi-automatic

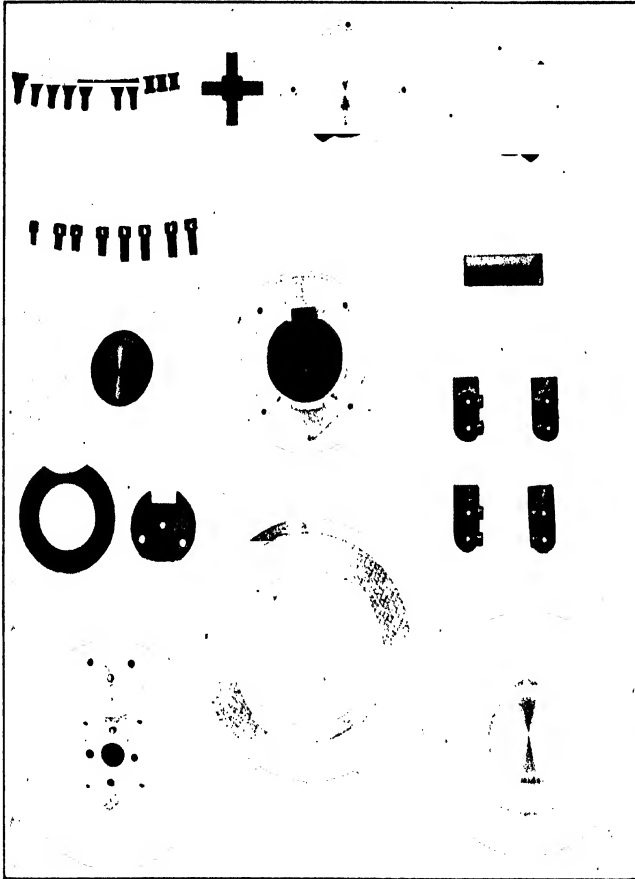


FIG. 35.—Parts of the mold shown assembled in Fig. 34. In the extreme upper left the inserts used are shown and in the upper right are front and back views of the molded article.

press and is provided with knock-out pins as shown at the right. The two parts of each mold come together without resort to a plunger of the type shown in Fig. 37B. At the bottom are the finished molded articles. An example of a positive or closed mold is shown in Fig. 39 which was designed for molding automobile steering wheels.

In this case the overhead portion or plunger telescopes with the body of the mold. In the outside wall of the plunger is an annular recess to receive any material extruded between plunger and body contacting surfaces. The "flash" or excess of material is thus collected

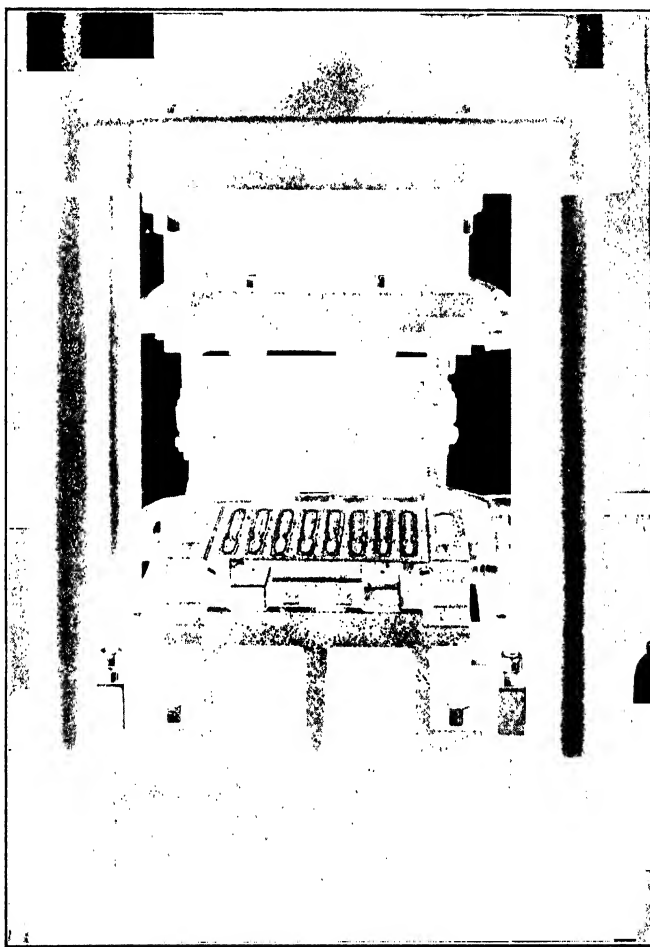


FIG. 36.—Direct-Heated Flash Type of Mold Mounted in Press.

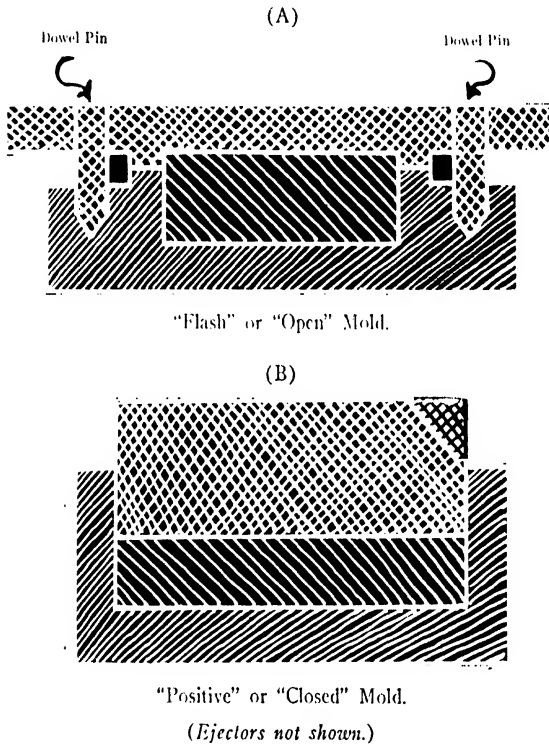
without causing the plunger to bind. Fig. 40 shows the finished steering wheel.

Methods of Heating Molds.

Most molds are heated indirectly by placing between heated plates in a hydraulic press. These plates or "platens" as they are called

may be heated by steam, gas or electricity, the first being decidedly the most efficient. Molds which are to be used for extensive production are usually cored and heated directly with high pressure steam. Such molds are illustrated in Figures 36 and 41. To the right and left of body and plunger may be seen the steam inlet and outlet pipes. Figure 41 shows an ash tray mold in a semi-automatic press.

FIG. 37.



Powder, Tablet and Sheet Stock Molds.

Molding compositions in powdered form are almost always molded in positive or closed molds. Occasionally, however, it is possible when molding a cup or a deep, hollow article with thin walls to employ a flash or open mold. For example, certain molds for distributors have been made of the flash type, permitting the operator more or less latitude in the weighing of his composition prior to charging the mold. When briquettes or tablets are employed a flash type of mold is almost invariably used. This is also true when sheet stock is to be molded. The powder mold requires a cavity large enough

to contain the required weight of composition and in using a filler of wood flour or asbestos it is customary to calculate the capacity of the cavity to be $2\frac{1}{2}$ or $3\frac{1}{2}$ times the final volume of the finished molded article. In the case of the tablet mold, since the molding powder has been previously compressed, a mold may be used having a cavity the size of the finished piece. In the majority of cases tablets permit the use of a flash type of mold where otherwise a positive type would be necessary. The advantage of this is readily apparent as

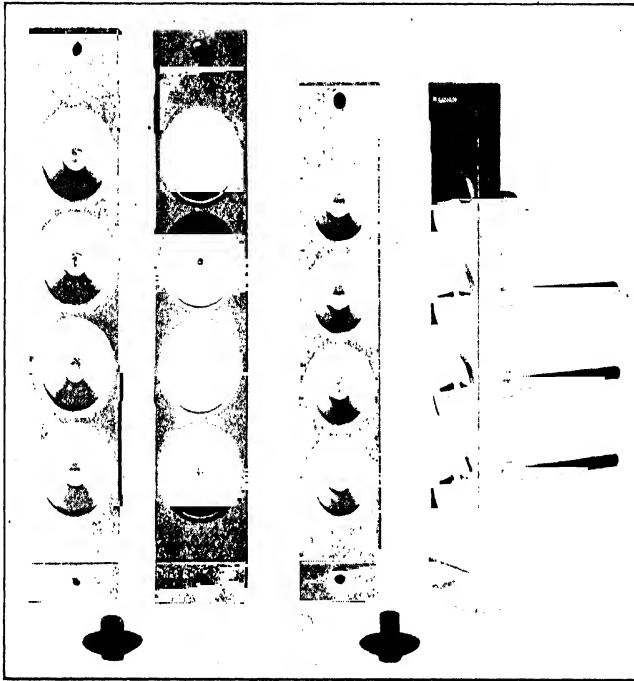


FIG. 38.—Flash Type Molds for Making Player Piano Roll Ends.
(Note ejector pins at right.)

it means less steel to heat up to molding temperature, lighter molds and lower cost in mold construction, in addition to the convenience and accuracy derived from the use of a tablet instead of a bulky powder which must be weighed for each molding. The sheet stock mold likewise requires a cavity only the size of the molded piece; and the sheet, previously softened by warming, is packed tightly into the mold.

Inserts.

Inserts are parts of a finished molded article which are of different material from the molding composition and which are set in proper

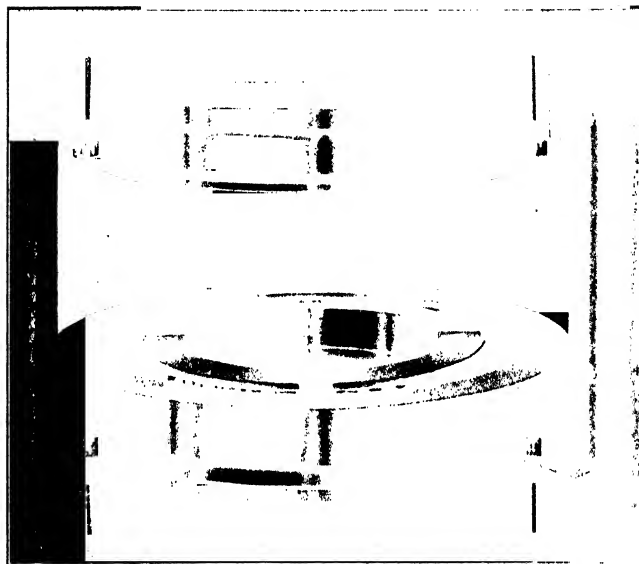


FIG. 39.—Positive Mold for Automobile Steering Wheel.

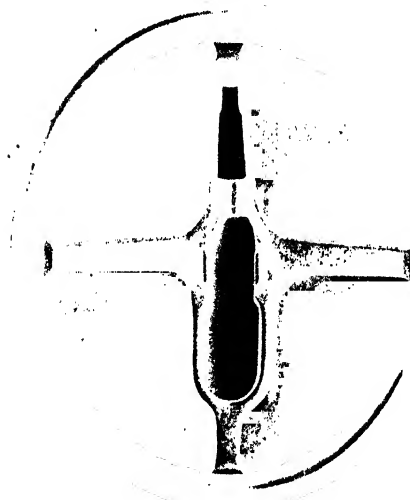


FIG. 40.—Steering Wheel Made in Mold Shown Above (Fig. 39).



FIG. 41.—Direct-Heated Ash Tray Mold.
(*Note steam connections.*)



FIG. 42.—Cross-Section of Automobile Distributor Head Showing Inserts.

place or positioned by the molding operation. Inserts may be of various metals such as steel, brass, copper, nickel, silver or may be rubber and in the case of rubber may be partially vulcanized in the molding operation. Inserts are usually anchored in some way to the mold. This may be done by means of a pin in the mold which fits into a hole in the insert or the insert may have a lug or a protruding pin which fits into a hole in the mold. Figs. 42 and 43 are cross-sections

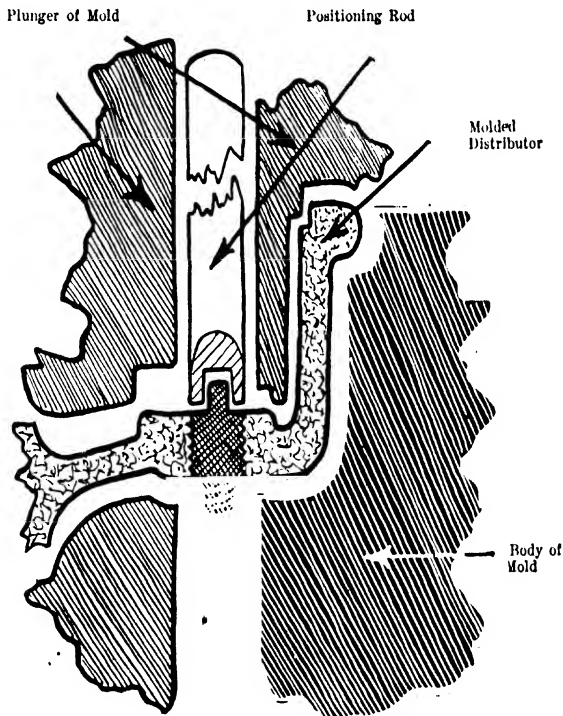


FIG. 43.—Diagram Showing One Method of Anchoring Inserts in Mold During Pressing. (*Clearance exaggerated.*)

showing metal inserts serving as contact points in a distributor head. In this case the lower ends of the inserts are fitted into holes in the bottom half of the mold and positioning rods or dummy pins extending into the cavity of the mold fit onto the heads of the inserts, thereby holding the latter in place and preventing complete envelopment by the composition while the mold is being charged and during the pressing stage. In the cross section shown the protrusions on the inside of the distributor are removed by placing the article in a lathe and turning down the metal ends.

Materials Used for Making Molds.

Hardened steel is perhaps the most universally used material for molds employed in plastic molding. Since the cost of designing, fabricating and maintaining molds is very high it is worth while in most cases to use hardened steel. Although the initial cost may be considerably higher than that of steel not hardened, the longer life of this type of mold and the lower cost of maintenance more than make up the difference in cost of fabrication. Hardened steel is economical especially when large quantities of articles are to be molded and when the design has been proved to be thoroughly efficient. In cases when a relatively small production is required or when the design of a mold is of doubtful efficiency steel, *not hardened*, is employed because in the making of the mold slight changes may be made easily in many cases. The *unhardened* steel mold, however, will require polishing oftener and if used in constant production will have to be discarded comparatively soon due to the wear and tear in general handling. In some cases gray iron castings have been used for molds where the peculiar or irregular shapes desired make steel difficult to shape. Gray iron castings are of course very brittle; cannot be well polished and their life is comparatively short. Molds for special purposes have been made of bronze and aluminum alloys and in the last few years in the molding of printing plates a "molded mold" made from synthetic resin with a thin metallic foil on the molding surfaces has been employed with satisfactory results. This type of mold has a very limited use.

Design of Molds.

The ideal mold calls for a number of features, all of which, in many cases, cannot be combined for various practical reasons. One or another may have to be omitted because of local exigencies. However in designing a mold the following points should be considered.

1. The hand operated mold should be as rugged as possible but be sufficiently light in weight to permit quick and easy handling. The small parts such as pins must be so protected as to prevent damage. Shoulders and sharp edges which come in contact with the plunger should be designed in such a manner that the shearing force will not damage them.

2. The mold should be easily assembled and dissembled and should therefore contain as few parts as possible. It is often desirable that the mold be charged from the top opening and discharged from the bottom and that the bottom discharge be made positive—that is, arranged to prevent the piece being discharged from the top. An advantage of bottom discharge is that the article is not marred by rubbing against the fin of composition which forms in the top of the cavity at the time of closing the mold.

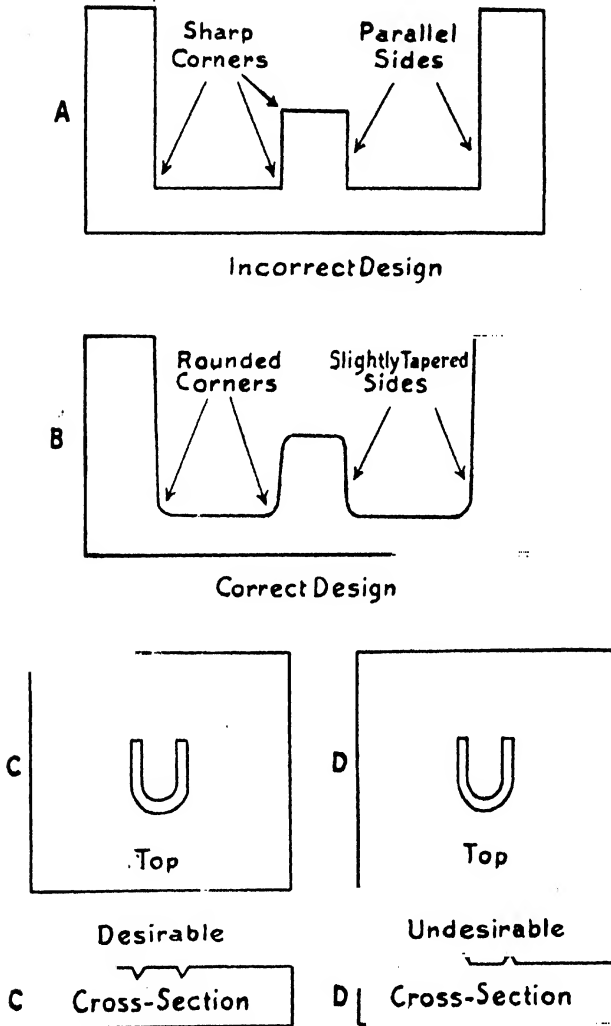


FIG. 44.—Showing Incorrect and Correct Mold Design.

Correct and Incorrect Designs.

It is advantageous to eliminate all sharp edges and sharp corners where the molding composition must flow. It is also well, when it is not absolutely necessary to have parallel sides, to make a slight taper or draft which greatly facilitates the removal of the finished

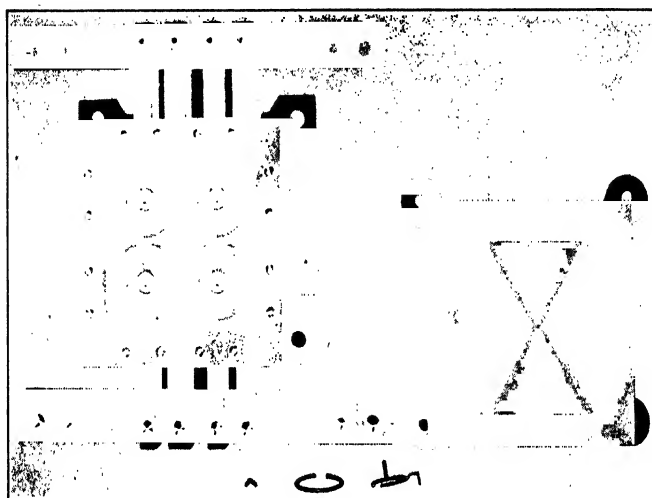


FIG. 45.—Illustrating Rounded Corners.

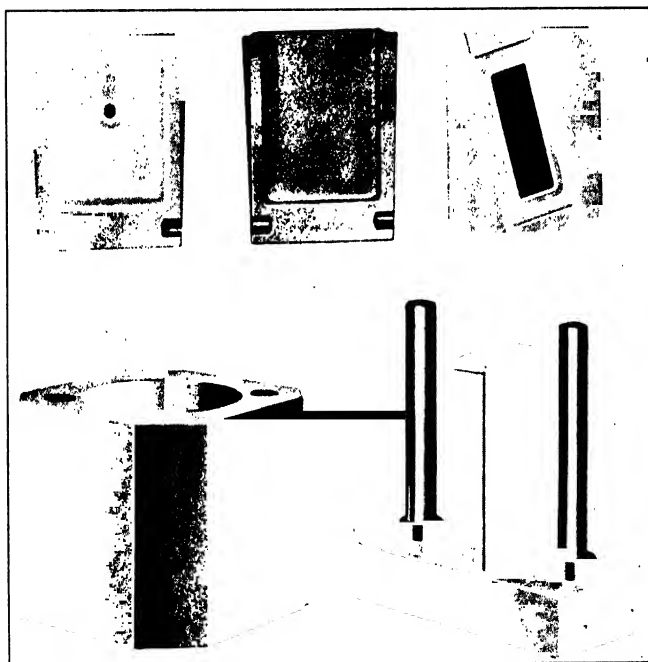


FIG. 46.—Illustrating Slightly Tapered Sides.

article from the mold. Fig. 44, A and B, illustrates the correct and incorrect design showing in Fig. A sharp corners and parallel sides and in B the rounded corners and slightly tapered sides. Figures 45 and 46 show molds with these rounded corners possessing the slight taper mentioned. It is also advantageous to have any figures or letters raised on the finished article rather than sunken because in the fabrication of the mold raised letters on the article require cutting or stamping into the mold merely where the letters or figures are placed whereas sunken letters or figures on the molded article require the removal, during the operation of making the mold, of the surface of the metal surrounding these. Furthermore the wear and tear in general use on these small protruding parts add to the cost of maintenance. Fig. 44, C and D, illustrates this point. Under-cuts should

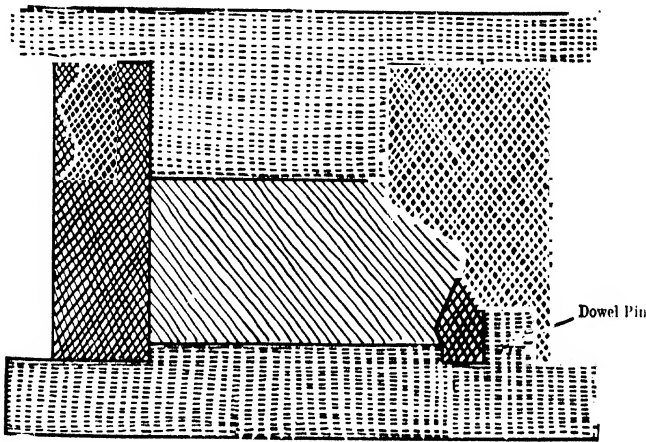


FIG. 47.—Example of Under-Cut in Mold Which Is Undesirable.

be avoided wherever possible. These are undesirable for the reason that they make molding much more difficult and the removal of finished articles laborious. Fig. 47 illustrates such an under-cut in the cavity of a mold.

Shrinkage Allowance.

It is possible in designing molds and in molding to make the pieces of very exact dimensions. In figuring on the dimensions of an article the shrinkage of the various molding compositions must be taken into account. It may be said that the ideal molding composition would possess just sufficient shrinkage to allow the articles to be easily removed from the mold. A shrinkage per inch of possibly one to two thousandths of an inch would probably be ample for this purpose. Molding compositions at present are not ideal as far

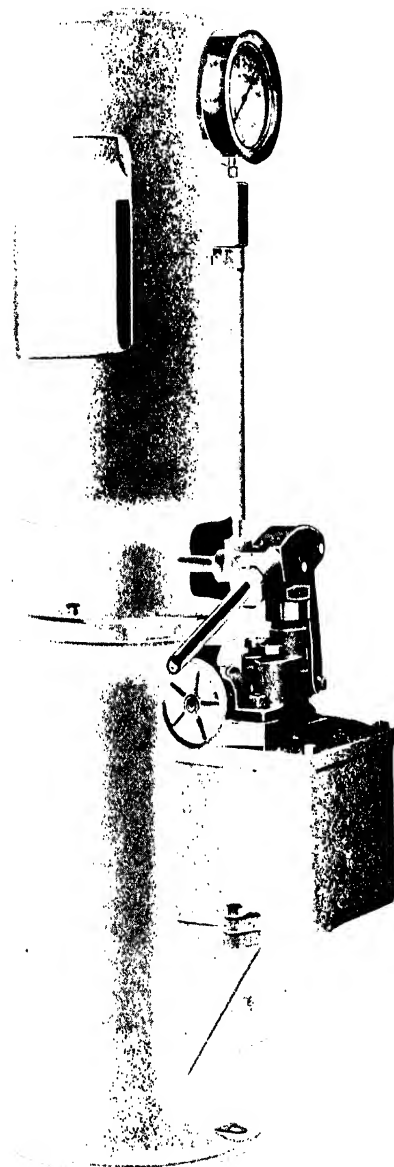


FIG. 48.—Hobbing Press.

as shrinkage goes. Those of the phenol-formaldehyde type average from four to six thousandths of an inch per inch of length or diameter. When a mold for a box with a tightly fitting lid is to be designed and likewise when pieces must exactly fit into a standard sized cavity in a piece of apparatus the dimensions must be very exact and allowance made for shrinkage.

Fabrication of Molds.

A well equipped machine shop including lathes, drill presses, shapers, profilers, milling machines, with their respective tools, engraving tools, etc., together with hardening and annealing equipment, is necessary for the fabrication of molds. Perhaps one of the most important of the special tools required for mold making is the hobbing press shown in Fig. 48. When a mold or several molds containing a number of impressions or cavities for molding the same article are to be made it is often desirable if only from an economical standpoint to "hob out" the cavities. This is done by forcing a negative or hob of the desired shape, which is made of hardened steel, into a piece of annealed steel by means of hydraulic pressure in a hobbing press. In doing this the annealed steel is first finished on the surface where the impression is to be made, the hob set in position upon the surface and pressure, ranging from 100-200 tons per sq. in., applied. The annealed steel then flows and takes the form of the hob together with the finish possessed by the hob. A great deal of skill is required in the performance of this operation and it is often necessary before the hob is sunk the correct distance to anneal the steel several times. By this method a number of impressions which are identical in dimensions may be made at a considerably lower cost per impression than would be the case if each cavity were machined out separately. Figs. 49, 50 and 51 illustrate a few articles, such as distributor heads, knobs, etc., which can be made in hobbled molds.

Molds are turned out with the same tools and in the same way as other articles from steel and the products are subsequently hardened by either the case or pack hardening process if low carbon steels are used or by quenching in oil or water when tool steels are used. Then they are finished by grinding and polishing with emery and rouge. The polishing of the hardened steel mold is largely a tedious and operation and a large proportion of the cost of molds is represented by this finishing process.

Repairs and Maintenance.

Careful handling of molds by the molder and the use of hardened steel molds greatly reduces the cost of repairs and general maintenance. The molds must be kept well greased when not in use, to prevent rusting, and free from abrasives which would mar the surface and require re-polishing of the mold. It is of course necessary for the molder occasionally to re-polish the molds after long use. It is not often

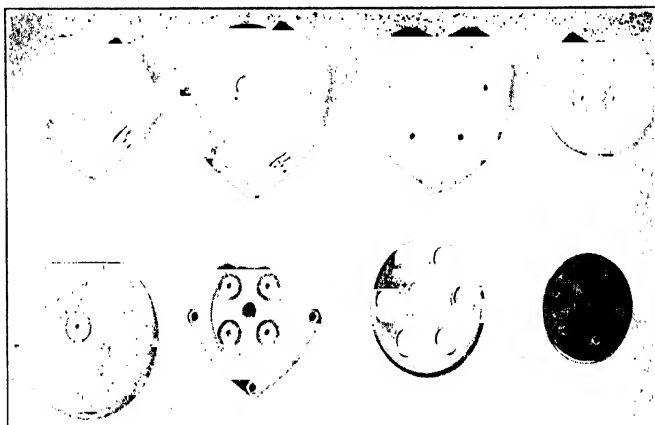


FIG. 49.

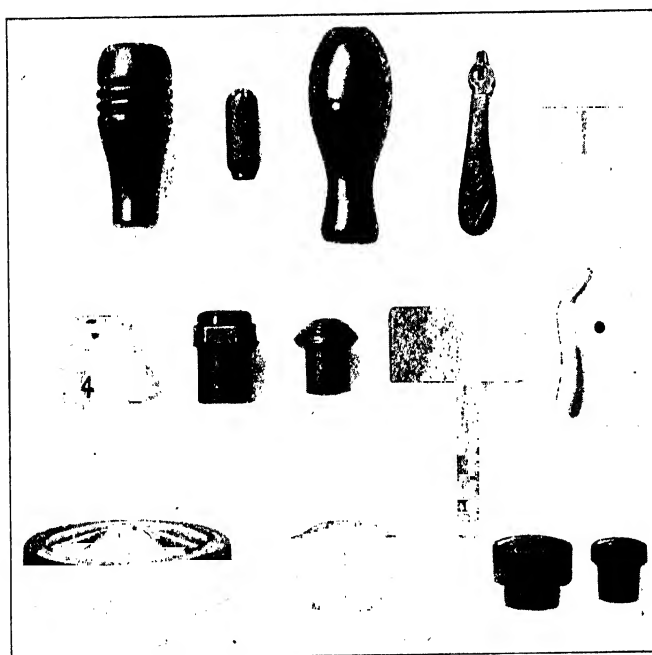


FIG. 50.



FIG. 51.

that the hardened steel molds are broken although this occasionally happens. Steel molds not hardened require more attention and their life is much shorter.

PRESSES.

General Construction.

Hydraulic presses are almost universally employed for plastic molding. Their construction is so well known that a description scarcely is required. However, for those who are not familiar with the parts of a hydraulic press, Fig. 52 will furnish the information required as it represents the plan upon which the hydraulic press is built. The essential parts of a press are a cylinder carrying a ram, the cylinder being a part of an open frame. The ram is forced out of the cylinder by means of a fluid forced into the cylinder by a pump. The top of the ram is equipped with a flat surface or device known as a platen and the under side of the head of the press frame opposite the end carrying the ram is likewise equipped with a platen. When the ram is forced out of the cylinder by means of a fluid pressure the movable platen approaches the fixed platen and a mold placed between them is subjected to heavy pressure. Water is generally used as the high pressure fluid and this is forced into the bottom or end of the cylinder through a small orifice. It exerts pressure over the large surface of the ram, thereby creating or building up a very heavy pressure. In hot presses the cylinder is copper lined and a packing is placed at the bottom or end of the ram so as to be as remote as possible from the heat. A high temperature shortens the life of leather packings. Figs. 52 and 53 show a heating press with the packing described. This is known as a cup packing. The copper lining also adds indefinitely to the life of the packing by presenting a smooth, non-corrosive surface contacting with the packing. Cooling or chilling

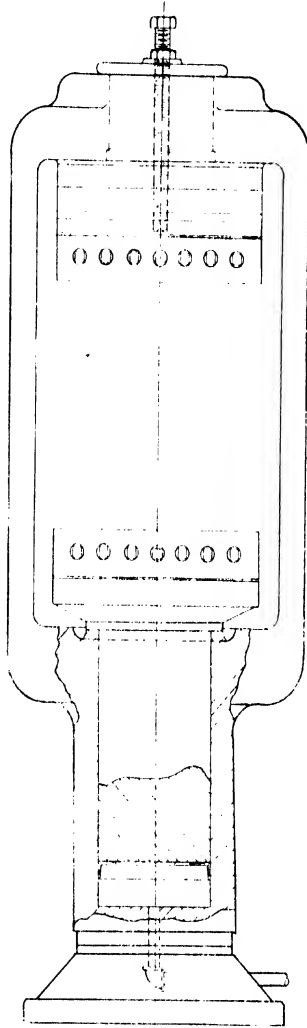


FIG. 52.—Diagram of Hydraulic Press.

presses are usually equipped with what is known as a "U" packing. (See Fig. 53.) This is set in an annular groove near the mouth of the

cylinder and so arranged that with an increase in fluid pressure the packing expands against the surface of the ram and the cylinder walls, and it becomes tighter as the pressure increases. This arrangement minimizes leakage.

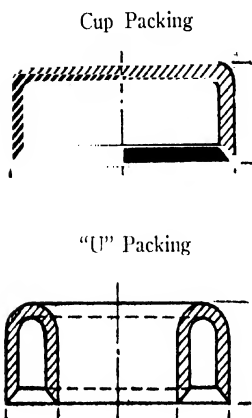


FIG. 53.—Types of Packing for Presses.

Platens.

The platens, which are mounted on the ram and head of the press, are cored to allow the circulation of either steam or water so that these devices may be quickly heated or cooled. In some cases the platens are heated by means of burners mounted in them, but this arrangement is rather clumsy and tends toward uneven distribution of heat. Electric heating elements are also sometimes used and are very desirable for small experimental presses. Steam for heating presses and molds is decidedly the

most efficient, not only because of the convenience and economy, but because of the excellent qualities due to latent heat. It is also necessary that the platens always be in exactly parallel planes so that the press should be devised to keep the platens permanently parallel, otherwise damage to molds will occur. The platens should be planed so as to present a smooth surface to the mold, as the more intimate the contact between the mold and the platens the quicker will be the heating and cooling process.

VARIOUS TYPES OF PRESSES.

Rod and Rodless Presses.

The rodless press, Fig. 54, is shown here in perhaps its simplest form. The head, sides, and cylinder of this press are cast in one piece of cast steel. The cylinder is lined, bored, and the head faced at one setting, thereby insuring the faces being absolutely square with bore. The rigid sides or uprights permanently maintain this condition which does away with all difficulty in the stretching of rods or loosening of nuts. This is of common occurrence in rod presses. Variation in the size of the opening can be obtained by inserting parallel spacer rings between the head of press and top platen. The type illustrated is extensively used for molding. This press is used for hot-pressing and is provided with a means of insulating the ram and the frame of the press from the heated platens, thus saving steam and protecting the packing. The press illustrated has a combination stop and release valve. One valve is connected to a high pressure water supply and when opened admits water under high pressure to the cylinder, thereby forcing the ram upward and closing the press. When it is desired to release the pressure this valve is closed. The second valve then is opened which releases the pressure in the cylinder and allows the ram to travel downwardly, opening the press. Fig. 55 illustrates a

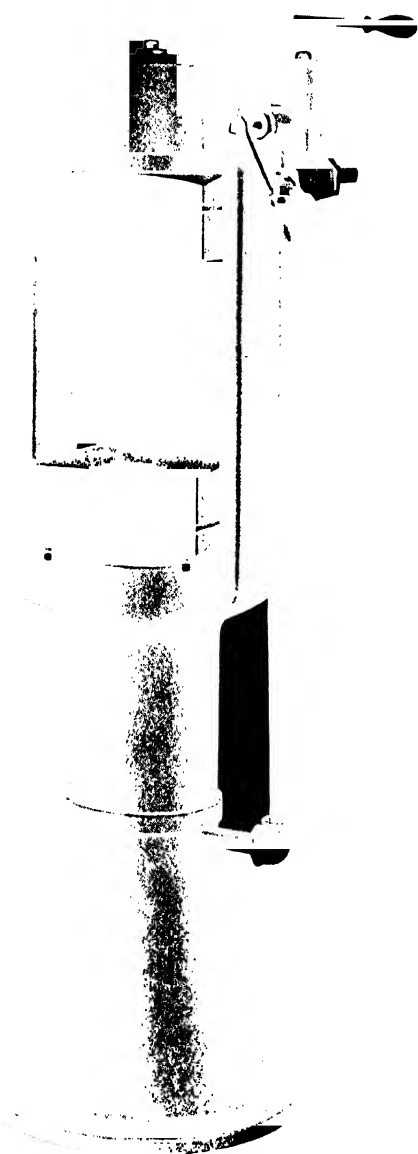


FIG. 54.—Rodless Press.

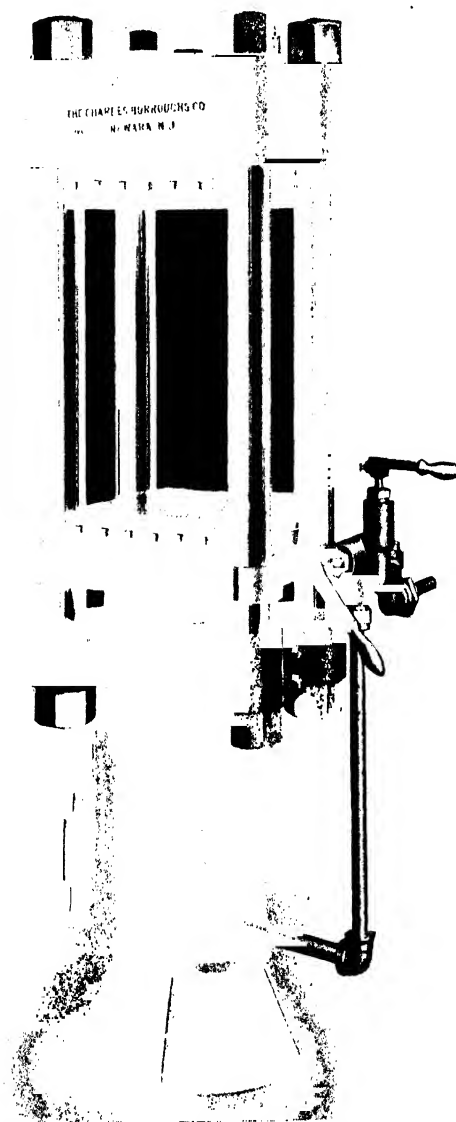


FIG. 55.—Rod Press.

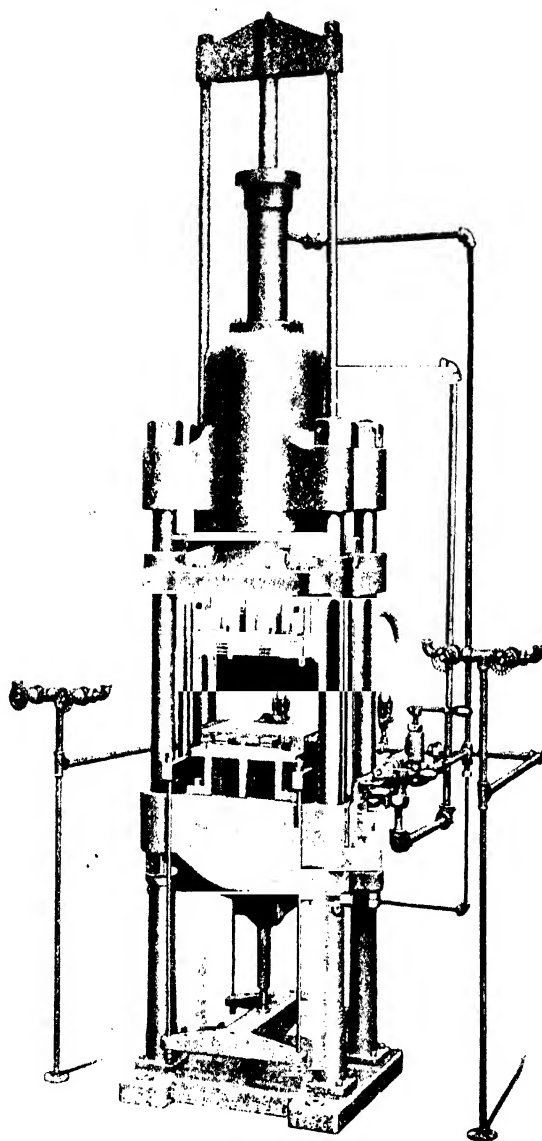


FIG. 56.—Semi-Automatic Inverted-Ram Rod Press.

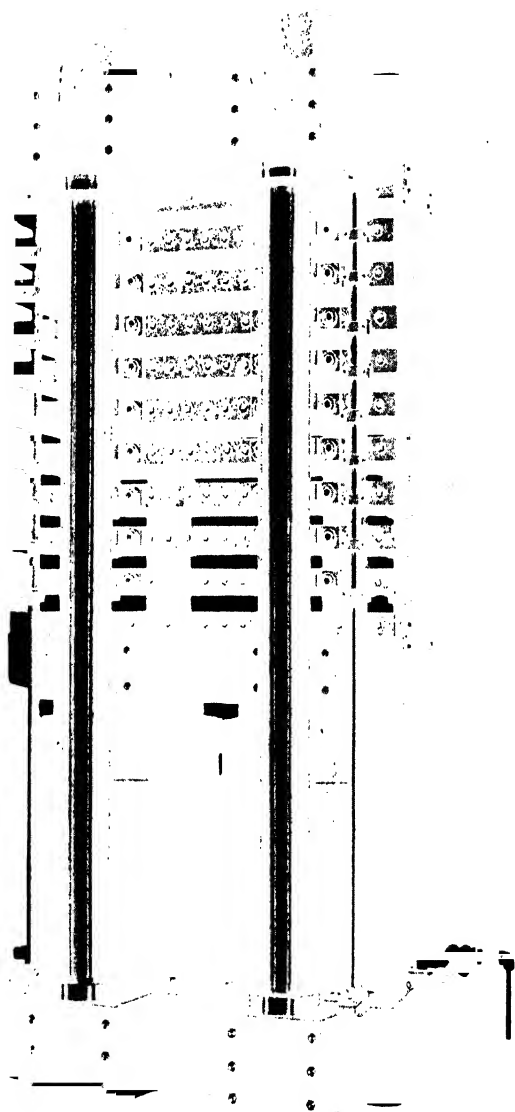


FIG. 57.—Multiple Platen Hot Press for Laminated Material.

typical rod press. This type of press also is in use in molding and its general principles are similar and the operation identical. Fig. 56 illustrates a semi-automatic inverted-ram rod press. This press differs from those shown in the preceding illustrations in that the ram and cylinder are placed at the top of the press applying the force downward rather than upward. The press is provided with a hydraulic pull-back which automatically pulls the ram upward when the pressure is released. Another feature, the knock-out pins, are automatically operated when the press is opened and eject the finished molded

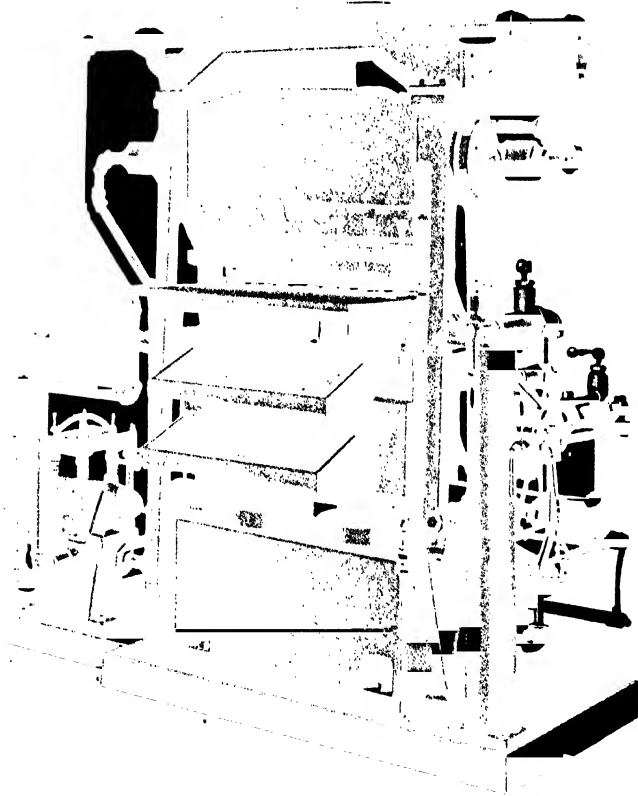


FIG. 58.—Automatic Molding Press in Operating Position.

articles from the mold. This is one of the first of the semi-automatic molding presses constructed, and is designed to have the mold direct steam heated and fastened in the press. The arrangement adds to the length of life of the mold as the latter is not subjected to the wear and tear of handling necessary in the case of hand operated molds. Automatic presses also conserve the strength of the operator and increase output.

Presses for hot pressing laminated fibre are built similar to Fig. 55, differing only in that they are usually much larger in capacity and are provided with multiple steam heated platens. Illustration 57 shows a press of 500 tons capacity with ten openings. The impregnated fibre is placed between polished steel plates and cured under high pressure.

Tilting Head Molding Press.

One of the most efficient and up-to-date presses for molding of both the fusible and infusible types of molding compositions is the tilting head press. Fig. 58 shows one of these presses in operating position. The molds for this press are direct steam heated, and the heating, cooling and press movements are controlled by valves on the column at the right of the press. On the left hand side is a hydraulically operated steam and water control which automatically admits the steam to the molds, thereby causing the fluxing and curing of the molding composition. A single turn of the valve shuts off the steam and

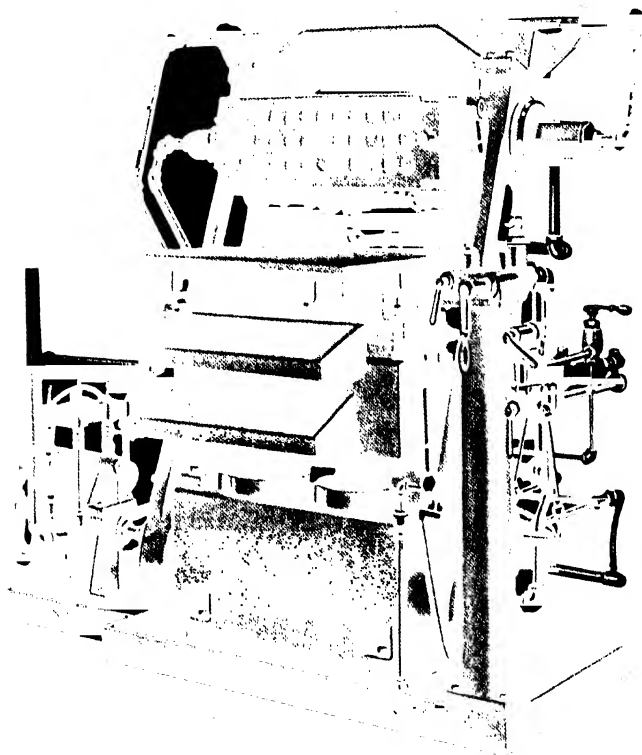


FIG. 59.—Automatic Press, Showing Head Tilted Into Open Position.

turns cold water into the molds. With this type of press and the direct heated mold it is possible to raise the temperature of the molding surface from room temperature to molding temperature in approximately 20 to 30 seconds. Fig. 59 shows the press with the top half of the mold tilted back to facilitate convenient inspection and necessary cleaning of the mold. The press is operated as follows: Steam is turned into the mold, the molding composition placed in the cavities, the press tilted into operating position as in Fig. 58, the press closed and pressure applied. This, as shown, is done by two hydraulic rams forcing upward. The tilting head construction enables the stroke of the ram to be materially shortened which makes for a substantial saving in high pressure water and greatly speeds up the opening and closing time of the press. After

sufficient time has been allowed for curing, water is admitted for cooling and the press opened. This press is equipped with automatic "pull back" cylinders and knock-out pins which eject the molded articles on opening the press.

Angle Presses.

Articles which are deep and hollow with threads, bosses, panels, etc., on their exteriors necessitate split mold parts held in a chase or retaining ring. This molding operation has been slow and consequently expensive due to the labor required in assembling and disassembling the molds. Much heat is required to effect the cure in these bulky molds and large quantities of high pressure water are needed to force the rams through a long travel. The angle press has greatly facilitated molding of this description. Fig. 60 shows a number of

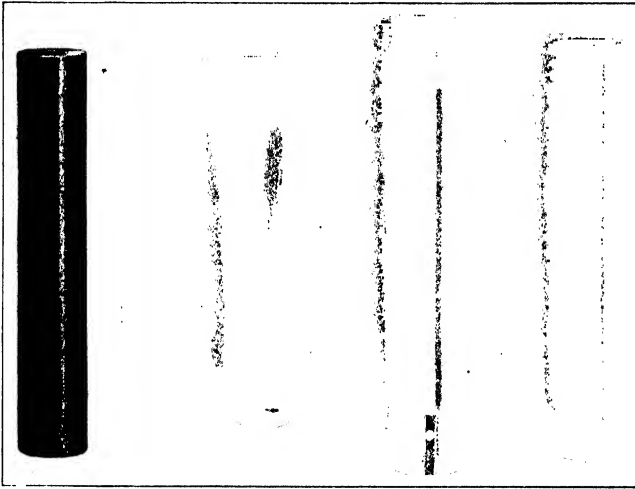


FIG. 60.—Types of Articles Which Are Best Molded in an Angle Press.

articles which may be molded advantageously in an angle press. Fig. 61 illustrates a typical angle press with telephone receiver shell molds mounted in the press. The molds are direct heated and the operation is as follows: The horizontal ram is allowed to close the bottom half of the mold as in Fig. 62. Steam is then admitted to the mold and the molding composition introduced into the cavities. The plungers of the mold are then forced into the cavities by a vertical inverted ram and the molding composition fluxed, cured, and cooled. The vertical ram is caused to move upward, thus withdrawing the plungers, after which the horizontal ram is moved back to its original position permitting the removal of the molded articles. This eliminates the use of retaining rings for split mold parts.

Pumps and Accumulators.

The hydraulic pump and the accumulator, although rarely seen in the molding shop, are perhaps two of the most important parts of the molding establishment. For small presses and especially when only one or two presses are being used, a hand pump is usually employed. This may be a separate unit or

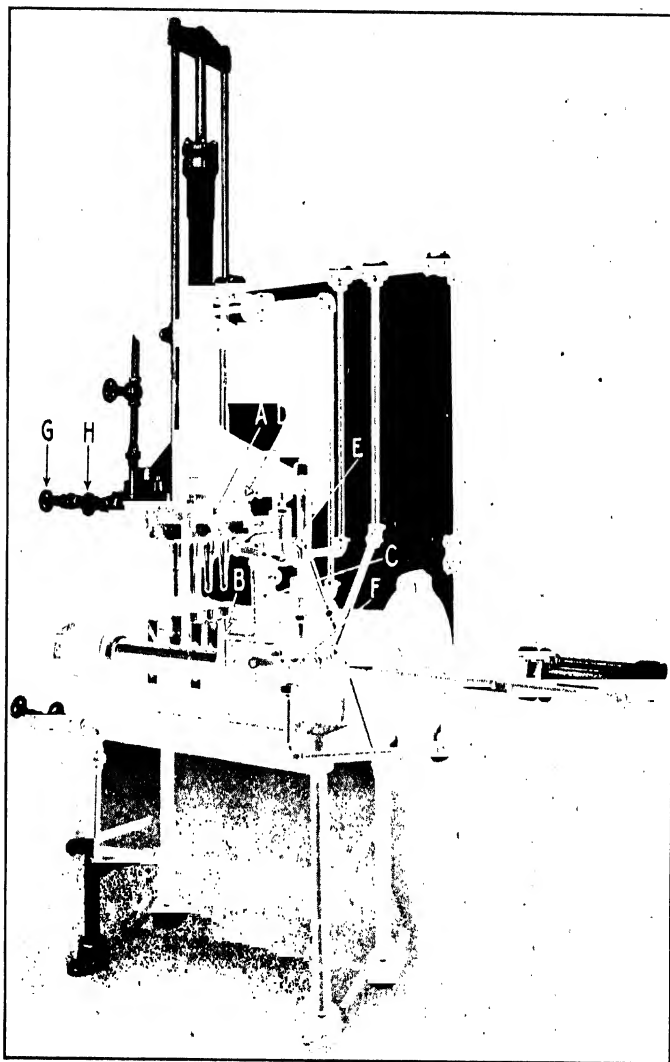


FIG. 61.--This illustration shows an angle press with the vertical ram A and the horizontal ram B in open position. A telephone receiver shell mold is mounted on the press and is heated and cooled by means of steam and water, controlled by valves G and H. Valves D and E control the operation of the vertical ram and valves C and F control the horizontal ram.

attached to the press itself, as shown in Fig. 48 of the hobbing press. When a number of presses are being operated, a power-driven pump of 2, 4 or 6 cylinder construction is employed. The pump may be constructed for use with or without an accumulator and may be provided with large bore cylinders which pump an abundance of low pressure water for moving the ram of the press through the idle portion of its travel. After the pressure rises to a given point these cylinders are automatically cut out of the system and smaller bore cylinders continue pumping to the desired pressure. When a pump is used without an accumulator, a by-pass valve must always be used to protect the pump and release the pressure when it becomes excessive.

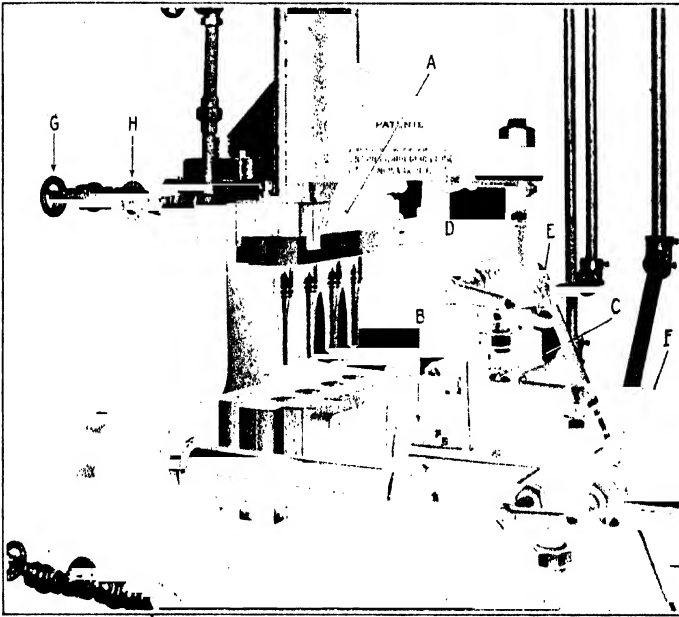


FIG. 62.—Angle Press. In this illustration the horizontal ram B of the press is closed and the vertical ram A is in open position, leaving the mold ready for charge of molding composition prior to pressing. The valves G and H control the steam and water for heating and cooling the molded parts. Valves D and E control the vertical ram and C and F control the movements of the horizontal ram.

Generally, however, an accumulator is used in conjunction with the pump as shown in Figs. 63-64. The pump propels water into the cylinder of the accumulator, forcing a ram upward. From the head of the ram are suspended a number of heavy weights. In order to raise the ram of the accumulator the pressure developed by the pump must be sufficiently high to lift these weights. When the ram rises to a certain point it trips a lever which cuts out the pump from the accumulator, allowing the pump to idle, and the accumulator is thus prevented from rising further. The cylinder of the accumulator is connected to the high pressure line which actuates the rams of the presses, therefore when the valve of a press is opened admitting the high pressure water into its

cylinder the water is withdrawn from the accumulator and the ram of the latter sinks. After sinking a set distance a second lever is tripped which throws in the pump and the water is forced into the cylinder of the accumu-

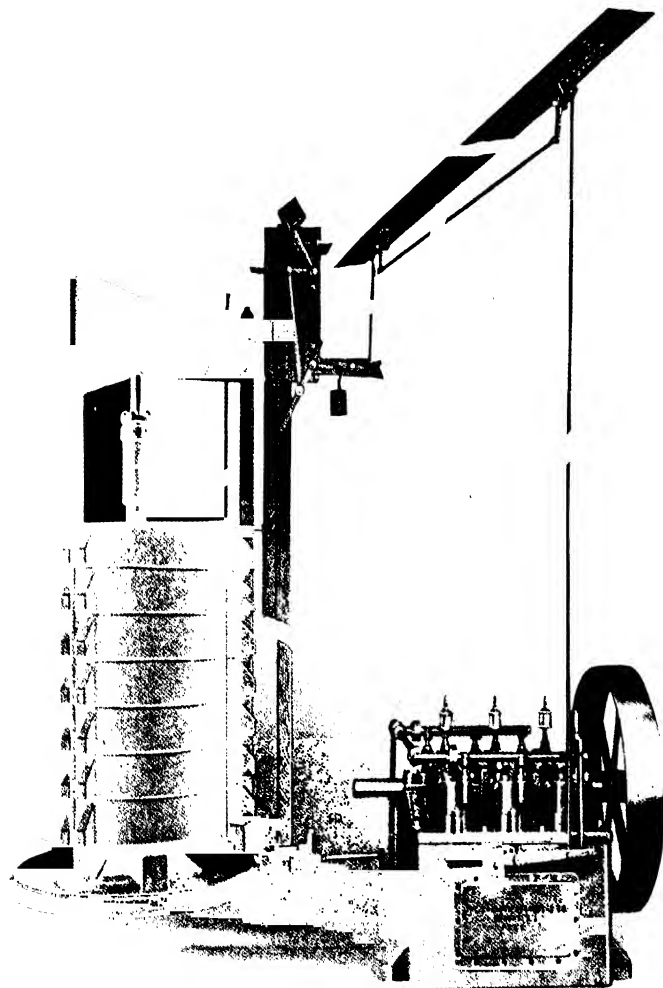


FIG. 63.—Hydraulic Pump and Accumulator.

lator again. In this way a constant supply of high pressure water is always maintained and the pressure may be regulated by attaching or detaching the weights suspended on the accumulator.

Hydro-Pneumatic Accumulators.

For certain situations an accumulator equipped with heavy cumbersome weights is not desirable and an "air loaded" accumulator is preferable. This

type differs essentially from the weighted accumulator by having the heavy weights replaced by air under pressure acting against a piston much larger than the hydraulic ram. The accumulator consists of two differential cylinders. (See Fig. 65.) A small hydraulically operated cylinder, which usually is a moving part on a fixed or stationary ram, forms the piston or plunger of a compressed air cylinder. The latter is connected to a heavy tank containing air at a pressure of 100-200 lbs. per sq. inch. In operation water is pumped into the small cylinder, which, when a sufficient pressure has been built up, is forced into the large cylinder, compressing the air in the storage tank. When the

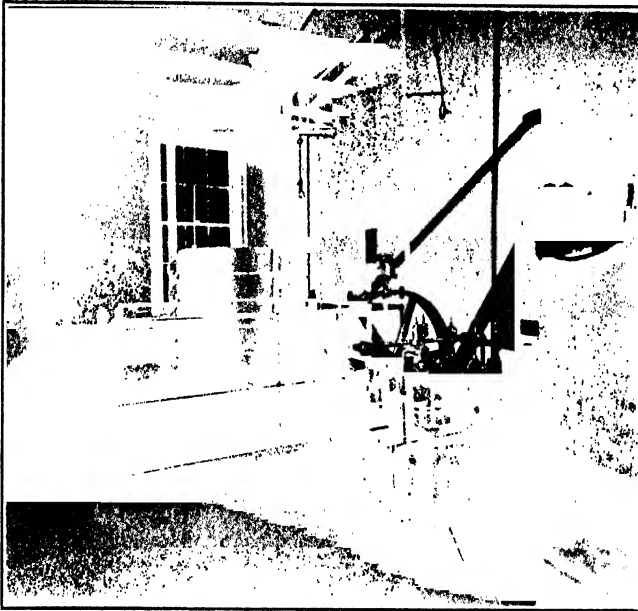
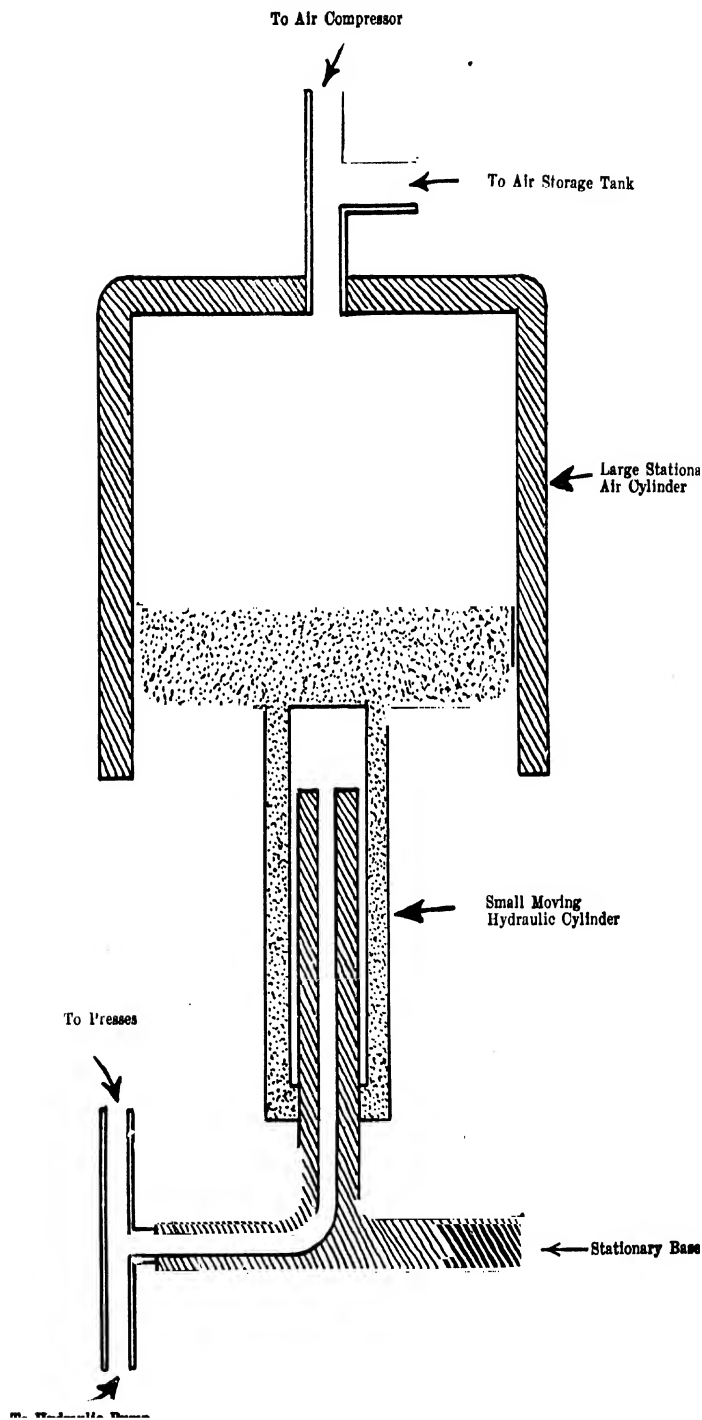


FIG. 64.—Typical Pump and Accumulator Installation.

stroke is almost complete a pump control lever (similar to that illustrated in Fig. 63) is tripped which allows the pump to idle. The return stroke of the accumulator throws in the pump and the operation continues indefinitely. The water for actuating presses is supplied from the hydraulic cylinder and is thus maintained at the desired pressure.

An air compressor is connected to the storage tank and is operated about once a day for a short time to maintain the pressure. By varying the air pressure the hydraulic pressure is regulated as desired. Several modifications are employed to suit the requirements. "Steam-loaded" and "water-loaded" accumulators likewise have been used.

Fig. 64 was provided through the courtesy of Mr. Frank H. Shaw, Shaw Insulator Company, Irvington, N. J.



Chapter 26.

Methods of Molding.

Fusible Resins.

In the molding trade two distinct types of molding operations are recognized. 1. Those involving the use of fusible resins such as shellac, rosin, copal and synthetic resins such as those made by the reaction of sulphur chloride or phenol. 2. Resins which harden in the mold by chemical reaction to an infusible condition. The present section is concerned with the molding of fusible resins, the hardening of which depends on cooling from the molten state and not on any reaction taking place in the mold. The temperature necessary for the molding of fusible resin compositions depends primarily upon the nature of the material to be molded. For example, shellac requires a temperature of approximately 150° F. As the shellac molding industry is highly developed and as its technique is applicable to the molding of fusible synthetic resin compositions a description of shellac molding will serve to illustrate the general practice in handling fusible resins. In shellac molding it is important to avoid excessive temperatures as too great a degree of heat causes a large number of rejects due to sticking, blistering and loss of finish. The molding of shellac compositions at least on the small scale, employing indirect heated molds calls only for a cooling press and a steam plate heated by steam at 60-100 pounds (usually 70 pounds) pressure. The shellac or synthetic resin is thoroughly incorporated with fillers and worked into the form of a sheet known as "sheet stock." The sheet is placed on a steam plate and is allowed to soften. Usually the molder places only a sufficient quantity of the composition on the plate to keep on hand just enough of the softened material to supply his immediate needs. This is especially true in the case of shellac which if heated for too long a time loses its valuable properties and forms a brittle worthless mass. The empty molds are heated by allowing them to stand in contact with the steam plate. The sheeted composition is cut approximately to size, allowing enough for overflow, placed in the hot mold and roughly formed to permit ready flowing. Then the mold is closed and is placed in the cooling press. The hot walls of the mold under pressure cause the softened composition to flow and take the required shape before the mold is sufficiently cool to harden or "set" the composition. The mold is then removed from the cooling press, opened and the molded article extracted and inspected; after which the fin or

flash caused by the extrusion of the composition along the separate parts of the mold is removed and the articles are polished. Fig. 66 shows a typical layout for fusible resin molding in small presses. The equipment is suitable for practically all of the fusible type of molding compositions, shellac being the most prominent. In molding shellac the labor required is highly skilled because of the peculiar properties of shellac which demand an unusual amount of experience in handling it. Another reason for the experienced man being required is that the production of a large number of molded articles with the smallest number of rejects requires a degree of dexterity which comes only after long handling of the material in a methodical manner.

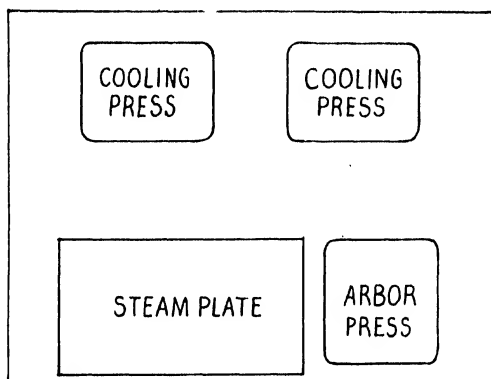


FIG. 66.—Floor Plan of Equipment Arranged for Molding Fusible Compositions.

Molding Compositions of the Type Which Become Infusible on Heating.

As has been stated previously, molding compositions of the type which become infusible on heating, or thermo-rigid, are handled in three forms, namely powder, tablets and sheeted material. In handling the composition in powdered form it is usually found necessary, especially when using positive molds, to weigh each charge accurately. In making small articles the molder will usually weigh to $1/64$ of an ounce. Before use the mold is heated as it is customary to charge the powdered material into a hot mold. After molding one article the mold is, of course, at a sufficient temperature to be used for subsequent molding without the necessity of preheating. The powdered material is seldom preheated and is usually charged into the mold at room temperature. Any inserts which may be required are placed in the mold prior to the introduction of the charge.

Pressures.

The pressures required for molding vary considerably but in comparison with those employed in the rubber and celluloid industry they

are high. If the average molder be questioned regarding the pressure used in molding synthetic resin compositions he will usually state this to be about one ton per square inch. Often the pressure applied is considerably in excess of that actually required for proper shaping of the material. The molder usually maintains on the hydraulic system a fixed "line pressure" best suited to the diameter of the rams of his presses. Therefore the molds are constructed for those particular presses and the molder may handle a dozen or more molds of various sizes during a day's run, in the same press, without the necessity of changing the line pressure. It is customary, however, in most molding plants to have a few presses with large rams and others with small rams in order that a higher or lower pressure on a mold may be obtained, if required, without changing the line pressure. A pressure substantially lower than one ton per square inch may produce a thick fin or flash which is objectionable and pressures greatly in excess of one ton may damage the mold. Low pressure is used for closing the press through the free space or operating clearance. Then high pressure is applied. The use of low pressure initially permits the material to distribute better, thereby placing less strain on the mold and preventing displacement or breakage of inserts.

Temperature Requirements.

The temperatures for molding compositions which become infusible on heating range from 300 to 450° F. (about 150-230° C.). For heating the platens of the presses most molding plants use steam at pressures of 80-175 pounds. This represents temperatures of approximately 300-375° F. (about 150-190° C.). Temperatures below 300° F. necessitate so long an exposure or cure in the press that these lower temperatures are not practicable. On the other hand temperatures higher than 375° F. usually call for chilling of the molds after the treatment in the press at such extreme temperatures. High temperatures tend to cause blistering of the molded article and sometimes bring about a pitting of the surface of the molded article which the molder will designate as "burning." The higher the temperature employed for molding the shorter the time of hot pressing. When, however, excessive temperatures are employed which necessitate subsequent cooling of the molds time will be lost in this way which compensates for the longer time in the press. At 350° F. (177° C.) most compositions which become infusible on heating can be rapidly cured and removed from the molds without special cooling. The time required for molding small articles at this temperature will range from say 2 to 10 minutes, the average time being 2 to 5 minutes.

Sheet Material.

The composition in sheet form is placed on a steam-heated plate, which is usually covered with a cloth or other means of partially insulating the sheets from the hot surface. The composition is

allowed to remain for a sufficient time to soften it somewhat. Then it is cut to the desired size, pressed into the mold by hand and the mass hot-pressed. Figures 36 and 38 are molds intended for use with a sheet material. Compared with molds employed for the powdered material it will be observed that these are shallow. An overflow ring or flash ring is usually provided. Fig. 41 illustrates a mold designed for the use of tablets. This also is more compact than that used for

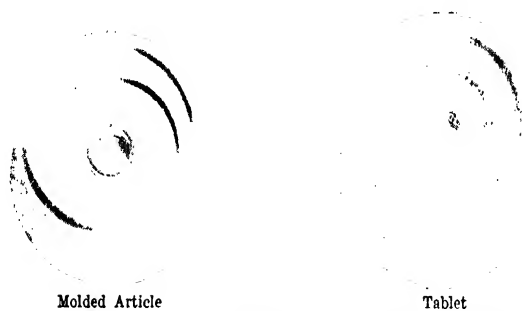


FIG. 67.

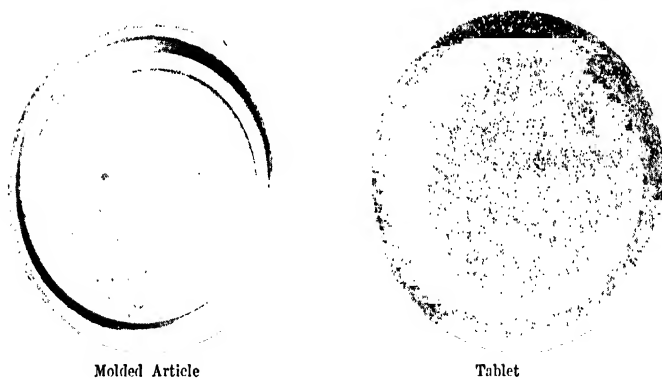


FIG. 68.

molding powdered material. Very beautiful mottled or striated articles may be made by mixing coarse fragments of sheet composition of different colors and molding the mixture.

Tablets or Briquettes.

Tablets or briquettes, as they are often called, are compressed cakes of molding composition prepared by subjecting to a relatively high pressure without heat, in a tableting mold, the requisite weight or volume of molding powder. The resinous binder is sufficiently plastic at this pressure to flow slightly and bind the powder to form a cake (see Figs. 67-68). The purpose of tablets is to permit the employment of a flash type of mold where a positive type otherwise would be

required. As the advantages of using a flash mold have been stated earlier in this chapter it is sufficient to say that the powdered or granular forms of the thermo-setting compositions have always been considered superior to the sheet stock because they cure faster and in the majority of cases may be removed directly from the hot mold, whereas the sheet stock usually requires at least a slight cooling. Tablets eliminate the labor, inconvenience, and waste of material occasioned by the use of sheet stock which must be carefully preheated on a steam plate and painstakingly packed in the mold. Tablets possess all the good qualities of the powder and in addition greatly increase the output of molded articles. It must be borne in mind, however, that the use of tablets involves the additional cost of tableting molds and the preparation of the tablets. When only a relatively small number of molded articles is required tablets are not practicable.

Tableting or Briquetting Mold.

A tableting mold should be designed to withstand a pressure of 5 to 6 tons per sq. in. on the molding surface of the plunger. It should possess a cavity very similar in shape to the cavity of the mold with which the tablet is to be used. The cavity dimensions with exception of the depth should be slightly smaller ($1/32$ "- $1/16$ "). The depth should be adjustable to permit the requisite volume of material (determined by trial) to exactly fill the cavity. The surface of the vertical walls should be sufficiently smooth to insure easy removal of the molded tablet. The molding surface of the plunger and bottom of ejector need not be so well finished.

Tableting or Briquetting Press.

Several "tableting machines" are in use in the molding industry which form tablets at a very low cost. These machines are automatic and operate similarly to pill machines. For a great many purposes they are satisfactory but for the formation of a tablet with "floating" inserts (that is; inserts temporarily held in place by the compressed material of the tablet), they cannot be used. Fig. 69 shows a tableting press which is hand operated and intended for a single cavity mold. There is provided a hopper, to contain the powdered composition, having a feeding device to fill the mold with the required amount of powder. This is operated by hand and arranged to slide back and forth over the mold. The latter is fastened in the press. The tablets are automatically ejected by opening the press. The output of this press is 3000 to 4000 tablets per day with a single cavity mold. A press of much larger capacity operating automatically is also built for preparing tablets.

Preparation of Tablets.

Tablets should be formed at a pressure of from 5 to 6 tons per sq. in. of cross area or at a sufficient pressure to enable the tablet to withstand, without crushing, the hot-molding pressure, i.e., 1 ton per



FIG. 69.—Hand Operated Tableting Press.

sq. in. Tablets so prepared will withstand handling in molding with no danger of breakage.

It is possible with the use of the press illustrated in Fig. 69 to form tablets having floating inserts as shown in the illustration, Fig. 70, of tablet and molded article. The usual placing of inserts in the mold and

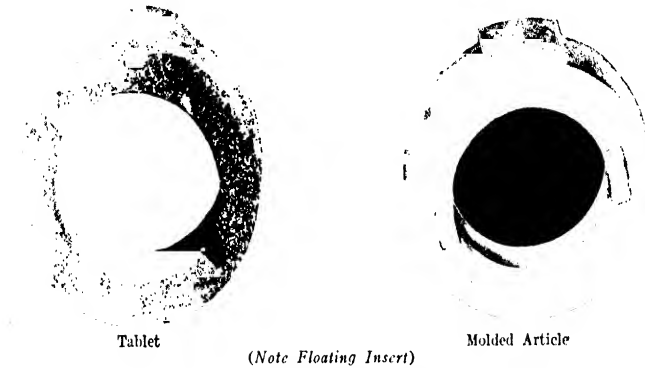


FIG. 70.—In this article a metallic ring is used as a floating insert. The ring does not show clearly in the tablet but is visible on the inner concentric surface of the molded piece.

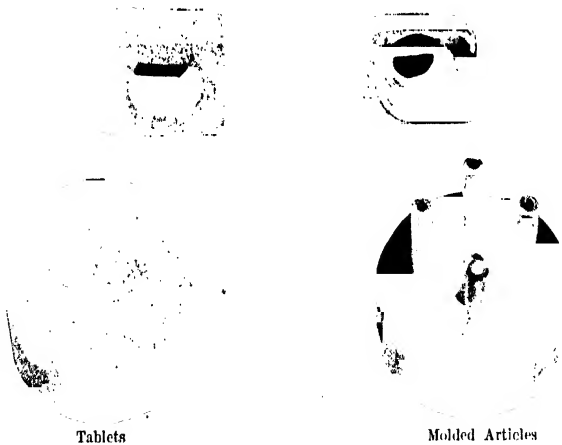


FIG. 71.

charging with molding composition, a time consuming operation, is simplified merely to the step of placing the tablet containing the correctly placed insert in the mold.

Tablets having one or more holes to fit over pins, positioning rods, etc., are easily formed. See Fig. 71, which shows the tablets and the articles molded from them.



FIG. 72.—Molding Procedure. 1. Weighing the Powder.



FIG. 73.—2. Charging the Mold (*direct steam heated*). This step is followed by closing the press slowly and then applying a high pressure which is maintained for several minutes.

Molding with Tablets.

Tablets may be used by placing in a mold and applying full pressure. The tablets are so compressed that they readily conduct the heat, quickly soften and flow. Molded products made by the use of tablets so prepared have a thin fin. It has been possible in some cases to remold the overflow from the hot-pressing of tablets since it does not receive the pressure necessary to render it sufficiently conductive of heat for cure. The spongy mass obtained as overflow may be mixed with fresh material and remolded.

The Molding Procedure.

The parts of the mold are forced together in a hot press initially, to good advantage, with a low pressure of about 500 pounds per square inch, followed by a final pressure of about 1 ton per square inch on the surface of the molded article. The initial low pressure prevents distortion of soft metal inserts. The final high pressure is applied to insure complete flowing of the composition and to cut off the flash or overflow. As will be later described the removal of the flash calls for a finishing treatment and the thinner this extrusion the less time spent removing it in the finishing room. Molding compositions of the phenol aldehyde type which have the property of becoming infusible by hot pressing ordinarily will require a long time of cure at temperatures in the neighborhood of 250° F. (121° C.). A cure will be effected very quickly at a temperature of 350° F. (177° C.), the time depending on the size of the molded article and especially the thickness of its walls or parts. Improvements in molding compositions and in the technique of molding have tended to reduce the time of molding so that articles which formerly required 7 or 8 minutes to cure now may be removed from the hot press in 4 minutes. After the complete curing, that is, hardening to an infusible product has been attained, the mold is removed. Sometimes it is placed in a cooling press for 1 to 5 minutes to chill the mold and facilitate removal of the molded article easily and without distortion. In other cases, however, the mold is opened immediately on removing from the hot press. This of course saves time in bringing the mold up to the molding temperature. A slightly better product, one having a higher polish, is obtained by the use of the cooling press and this step is desirable when manufacturing cost will permit. The molds may be opened by means of an arbor press or may be sufficiently easy to open by hand. The best method of handling the molds is found only by experience and the removal of the molded articles is a procedure which must be worked out for each mold as a separate problem. In some cases the articles may be loose and drop freely from the mold. In other cases it is necessary to use a knock-out pin for removal. The molder who is handling compositions of the thermo-setting or infusible type and working with molds which are indirectly heated usually handles two or more molds. In this way while one mold is in the hot press for the curing process the

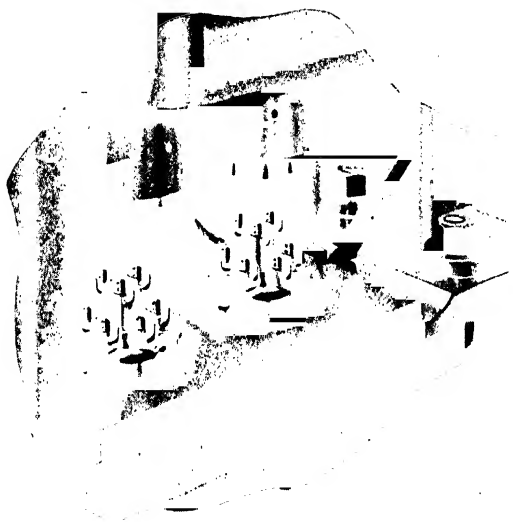


FIG. 74.—3. The Press Is Then Opened and the Molded Articles Automatically Ejected.

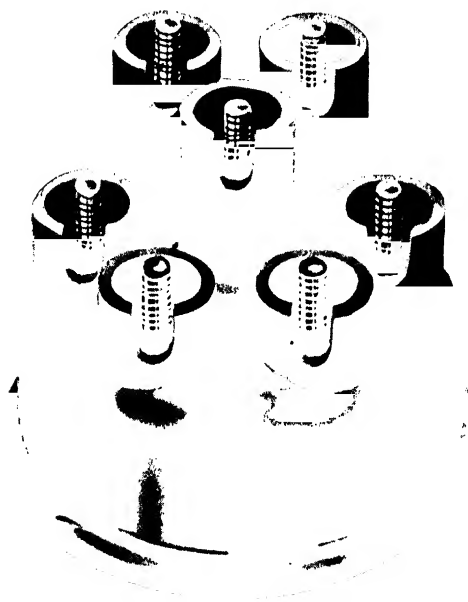


FIG. 75.—The Finished Article as It Comes from the Press.

molder may be re-charging and removing pieces from other molds. When automatic presses are used, such as the tilting head type, it is often possible for the molder to operate two presses, even though curing in these presses is rapid. Because of the automatic features of this style of press time is saved and may be spent in operating a second press. Figure 76 shows a typical arrangement for molding with indirect heated molds for molding compositions of the thermo-setting or infusible type. The molder works at the steam plate shown which has a wooden shelf at the back of the plate for tools, inserts, scales and molding composition. In front of the plate is a wooden ledge serving to protect the operator. The presses are placed in back of the

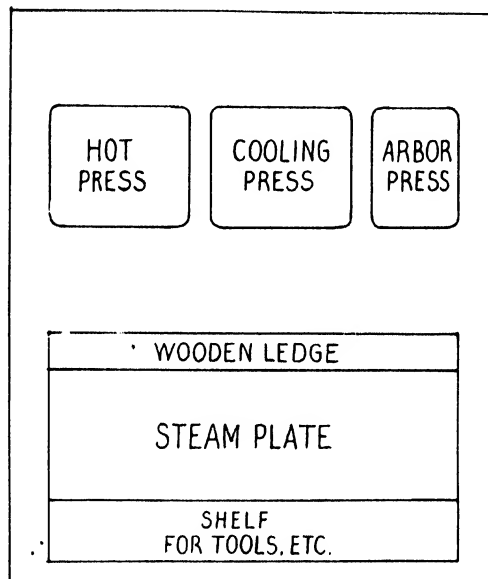


FIG. 76.—Floor Plan of Equipment Arranged for Molding Thermo-Setting Compositions.

molder and may consist of a hot press, a cooling press and an arbor press, or possibly two hot presses, the cooling press being omitted. The molded articles are placed in boxes at the end of the steam plates. When filled, these boxes are removed to the finishing room.

General Handling of Molds. Cleaning.

Good molding cannot be accomplished with dirty molds and it is therefore imperative that the molds be kept absolutely clean. Most molding compositions are of such a nature that they serve to keep the mold well cleaned and polished and on removal of the molded

article the only material remaining in the mold will be flaky particles which come from the fin or flash. Occasionally, however, when inserts are being used and when the parts of the mold do not fit tightly, some of the material may lodge in crevices. This may readily be removed either by a compressed air blast, which is often piped to each molder's steam plate, or by means of a brush or rag. Molds are very seldom charged while cold, preheating being the practice, the mold temperature being kept as high as practical for the work to be done. Positioning rods when used should be cold and may be cooled in water before insertion. The removal of the pins is greatly facilitated by keeping their temperature as low as possible. Inserts on the other hand are usually placed in the mold in advance of the molding composition and thus have opportunity to become thoroughly heated, which insures a good bond. In the charging of the mold with powder it is frequently necessary to tamp the material down thoroughly in order to get a sufficient amount into the cavity. After this is done the mold is closed by inserting the top half or plunger. Molds usually have dowel pins to serve as guides and to insure alignment. These are greased slightly from time to time to permit ready removal and to prevent the molding composition from sticking around them. The opening or discharging of the mold is often effected by means of ejector pins or "spiders" which fit into holes in the mold and force the sections apart.

General Discussion of Difficulties in Molding.

It has often been said by molders, and it is undoubtedly true, that each new mold is a new problem in molding which can be solved only by actual experiment, aided of course by general observation and experience in molding. When a molder receives a new mold and puts it into operation he considers himself very fortunate indeed if the first molding or "heat" results in a perfect molded article. It is very seldom that this occurs and at least five or six heats are usually required before a good article is obtained. Sometimes a molder may work for a whole day or more before he finds a method of molding which is suitable and turns out pieces with only a moderate number of rejects. It is impossible to state here all the causes of difficulties in molding. Troubles may arise at any time due to peculiarities of the material or mold which is being used. It is possible to discuss only the usual troubles of the molding plant. Of these main difficulties; sticking, staining, blistering, and flow marks may be included.

Sticking to the Mold.

Sticking is the adherence of the compositions to the mold, making difficult the removal of the finished article. Also the surface of the mold is soiled and there are left in the molded articles roughened patches without gloss in the places of adhesion. From time to time practically all molding compositions give more or less difficulty from sticking and this trouble is one which frequently engages the attention of the

molder. Certain manufacturers of phenol-formaldehyde resins state that they have practically overcome this difficulty by the employment of a special lubricant in the composition and strongly advise against the use of a lubricant applied to the mold. It is not always easy to trace the cause of sticking and at times a plant may be subjected to considerable annoyance due to this difficulty. With compositions which are permanently fusible, sticking may be due to the removal of the molded article while too hot, molding at an excessive temperature, use of a dirty mold, or to some defect in the composition employed. In the case of the infusible or thermo-setting compositions sticking may be due to under-curing, too high a temperature for molding, or to the composition itself. The phenol-formaldehyde resins, according to the manufacturers, can stick to the mold only under three conditions. Either the composition is undercured, the mold is of improper design, or the composition is itself defective. In view of the several causes of sticking it will be evident that the problem frequently requires special study. In general, with infusible or thermo-setting compositions, sticking is due to the composition itself oftener than to manipulation. Sticking often may be remedied by applying to the mold a small amount of a lubricating substance such as machine oil, grease, stearic acid, ceresin or paraffin wax. There are also on the market special "molding oils" which are useful. Sometimes these contain a solid solvent for the composition and a hardening agent. Only a very small amount of lubricant should be employed and this may be applied directly to the mold with the aid of a brush.

The use of lubricants is not thoroughly understood by most molders and it is not always possible to obtain consistent results with the same composition in different molds. In many cases ordinary machine oil or petroleum jelly is effective in preventing sticking. In other cases machine oil will cause the surface of the molded article to be spotted and better results may be obtained by using a lubricant which is a solid solvent for the binder of the molding composition. Manufacturers of molding compositions have given the problem of sticking a good bit of study and most of the ready-prepared compositions on the market contain a lubricant of one kind or another. However, the ready-prepared compositions at times give trouble from sticking, hence the molder requires to be familiar with methods of lubrication of mold surfaces.

Staining.

Staining is a discoloration of the metal surface of the mold and of the surface of the molded article, occurring during the molding operation. Stains are usually caused by the action of the molding composition but may possibly occur from overheating or, in the case of some infusible compositions, from opening the mold before the composition has been sufficiently cured. Stains from overheating are usually attributed to the decomposition of some ingredient of the molding mix, the products of decomposition attacking the surface of the

mold. The obvious remedy in this case is to conduct the molding operation or curing at a lower temperature and to increase the time of curing accordingly. If the staining influence is a vigorous one the action will show very quickly. On the other hand staining may progress very gradually and not be noticed until several hundred articles have been turned out from the mold. Molding compositions frequently contain stearic acid in small amount functioning as a mold lubricant. This acid, especially in cruder form, has been observed to cause staining in some cases. The stain or corroded spot on the mold affects the surface finish of the molded article. If a brilliant glossy surface is required on the article the mold itself must possess a high polish. Any stain or spot on the mold, no matter how slight, will be transmitted to the molded article and, in fact, stains or scratches scarcely visible on the surface of the mold will show very clearly on the molded article. For example, by writing with a pencil on the surface of a mold very little indication of the writing will be observed but on the molded article the transmitted writing appears on the surface very distinctly.

Stains on the surface of the molded article may be due to a dirty mold or in some cases, especially with sheet composition, to the application of pressure too rapidly before the material has reached the proper temperature to flow readily. Fine lines on the surface often indicate that the composition has been overheated before applying pressure, thereby causing the reaction to proceed beyond the point which permits the material to flow freely.

Blistering.

Blisters in molded articles are produced by the expansion of gases or vapors formed or liberated during the molding operation. The blisters may be small and distributed throughout the article or one or two large blisters may form well below the surface. In any event the appearance and strength of the article is seriously affected by blisters. With compositions of the permanently-fusible type blisters are due usually either to conducting the molding at too high a temperature or to opening the mold before it has been cooled sufficiently. If, after adjusting these two factors, blistering occurs the composition should be examined. The latter may contain moisture or solvents used in its preparation and further drying may eliminate the difficulty.

With compositions of the thermo-setting or infusible type when molding is conducted at a temperature not exceeding 350° F. (177° C.) blistering is not likely to occur from any lack of proper technique of molding but is more likely traceable to the composition. In this case the composition likewise may retain moisture or solvents which expand from the heat of the mold. However, the use of an excessively high temperature and subsequent opening of molds without any cooling may cause blistering. An insufficient time of curing sometimes will cause blisters and in most cases the adjustment of the molding temperature and increase in the time of cure will eliminate

this difficulty. The use of a cooling press adds one more step in the manipulations of molding and it should be unnecessary thus to cool the thermo-setting type of composition when molding is carried out at a platen temperature not exceeding 350° F. (177° C.). For pieces requiring accurate sizing this does not hold true as they tend to warp and vary in dimensions unless cooled under pressure.

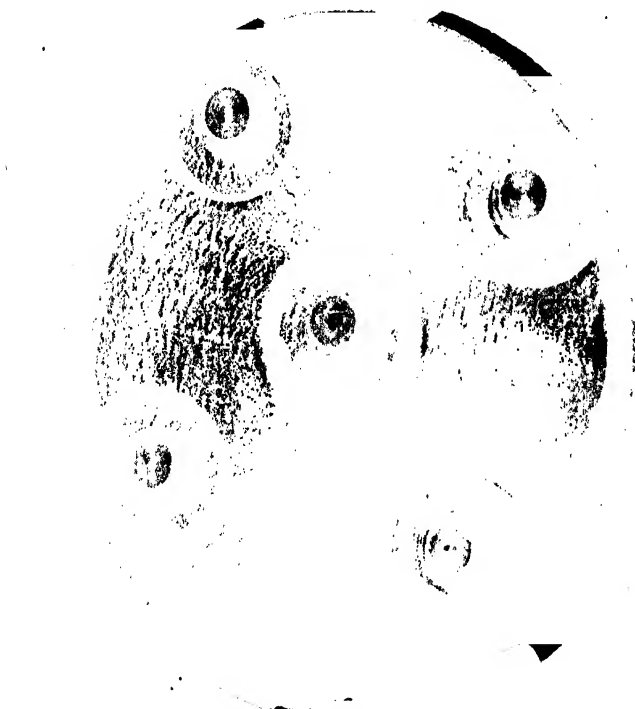


FIG. 77.—Example of Flow Marks on Surface of Molded Article.

Lack of Flow.

Flow marks are periodic, light and dark cirrus-like markings in the molded article. They are at a 90° angle to the direction of flow.

Flow marks are due to insufficient plasticity of the composition at the temperature employed for molding. The composition may not be hot enough to flow when pressure is applied or it may be so far reacted before applying pressure that plasticity is lost. This occurs with the thermo-setting composition when sheet stock or tablets are insufficiently heated or overheated before pressing. Fig. 77 illustrates a molded distributor with flow marks on the surface. Sheet stock which has been over-reacted will often show seams where pieces of

the sheet have welded together. Careful preheating of the tablet and sheet composition and adjustment of the temperature and pressure in molding should eliminate this difficulty unless the composition is defective.

Undulated Surface.

A rippled or uneven surface on molded articles made from compositions which become infusible on heating is attributed by some observers to the evolution of gases which form pockets between the mold surface and the material which is being molded. These very slight undulations are readily visible when examining the article by reflected light. Whatever may be their cause it is generally understood among molders that chilling the mold before opening will usually remedy the fault. Furthermore the defect is not considered a serious one and the molder often is willing to condone a slight unevenness of surface to avoid the extra time taken in the manipulations of chilling the article. The author has observed the formation of this undulating surface in molding compositions having a phenol-formaldehyde condensation product as a binder and also those containing an acetone resin binder capable of hardening on heating to an infusible product.

FINISHING AND INSPECTION OF MOLDED ARTICLES.

Machinery and Other Materials.

The finishing and inspection room of the molding shop is equipped with lathes, buffing wheels, polishing wheels and abrasives such as rouge, emery, tripoli and often a number of other of the softer abrasives. Buffing wheels used for the purpose are generally made of canvas and some of these are treated with an abrasive which has sharp cutting qualities. Treatment of this sort gives what is termed a "hard wheel." The use of a very mild abrasive or of grease alone gives a "soft wheel." Hard and soft wheels for the infusible and fusible types of molding composition are always at hand. Perhaps the biggest task of the finishing room is the removal of fin or flash so as to leave as little trace of them on the molded article as possible. If the article is round it may be placed in a lathe and a file lightly applied to trim off the fin and leave a smooth surface. If the fin is not heavy and is on a straight surface it may be removed by buffing or by means of a sandpaper belt. Sometimes the operator must resort to filing the fin off by hand. This is usually done with fins in odd-shaped pieces but in general the practice in molding is to make the fin as thin as possible so that very little labor in finishing is required. The fusible or shellac type of molded articles are polished by means of a *soft* wheel which is greased but has no abrasive. Here again if the article has a round surface it may be possible to construct some sort of holder to allow the article to spin around as it comes in contact with the polishing wheel. The infusible type of compositions are usually buffed on a

hard wheel with tripoli followed by polishing on a soft wheel which carries no abrasive. Inserts occasionally need to be machined after the article has been molded. This is usually done before the buffing and polishing and may require drilling or turning in the lathe. Or the buyer of the molded article may prefer to do the machining, in which case the molded articles are shipped to the buyer without the customary buffing and polishing. Finally the articles are inspected for imperfections and packed for shipment.

COLD MOLDING.

As the caption implies articles made in this manner are molded in the cold. The operation is, however, far from complete with mere molding or shaping. The articles require careful and protracted exposure to heat to harden the binding agent. A vast quantity of small shaped articles are made by the cold molding process. The prime requisite here is cheapness rather than quality. In fact, the outstanding feature of cold molded products is their cheapness. In the past, synthetic resins have not played a prominent rôle in the production of cold molded parts as the cost of these resins in comparison with the asphalts and pitches generally used as binders was too great. It is true that shellac is sometimes used as a binder in making cold molded articles but this resin is being largely displaced by the relatively much cheaper pitches and asphalts. In recent years resinous phenol-formaldehyde condensation products have found a limited use in cold molding operations and their application in this direction is increasing. The resins obtained by the condensation of phenols with furfural have given promising results in cold molding. However, owing to the limited use of synthetic resins in cold molding, the scope of this volume precludes any detailed description of the various methods employed in carrying out molding in the cold.

The cold molding process was pioneered in the United States by Hemming, who started the industry here in 1909. Its development has been rapid and the process now represents one of the most important methods of commercial manufacture of heat resistant plastics prepared with organic binders. For further details consult Hemming, "Plastics and Molded Electrical Insulation," New York, 1923.

Uses of Cold Molded Articles.

Articles made by the cold molding process are devoid of the smooth glossy surface finish characteristic of articles made by hot pressing. The surface of the article is usually dull and rough and requires a considerable degree of buffing to afford an attractive appearance. One large outlet for cold molded articles is in the field of electrical insulation and other purposes where a high resistance to heat is demanded. The baking or "stoving" treatment develops a resistance to heat quite

lacking in articles made, for example, from shellac or other fusible resinous binders and indeed secures a substantially greater resistance in most cases than can be obtained by hot pressing resinous phenol formaldehyde condensation products. The exactness of dimension and mechanical perfection obtained by the more costly process of hot pressing are lacking in cold molded articles but in many cases the products are intended for use in enclosed electrical equipment where the appearance is not a matter of consequence but where resistance to heat and cheapness of manufacture are considerations of importance.

Binders and Their Solvents.

The usual binder employed in cold molding operations is a pitch or an asphalt. Coal tar pitch admixed with gilsonite is a useful binding composition. The mixture is dissolved in a composite solvent. This is made up of a light volatile solvent such as benzol and a heavy solvent of which anthracene oil is representative. The light volatile solvent serves to dissolve the pitch and gilsonite forming a solution having good penetrating powers, thereby easily mixing with the filler employed. The purpose of the heavy solvent is to keep the material plastic on exposure so that it will not dry out completely when kept adjacent to the presses during the day's run of molding. Enough solvent is present to render the composition plastic or slightly moist, permitting rapid molding. The material is not dried to remove light solvent preparatory to pressing.

The better grades of cold molded compositions having an asphaltic base frequently contain varying proportions of a drying oil. Linseed, Chinese wood and fish oils commonly are employed. The addition of stearine pitch also is considered beneficial.

Fillers.

A filler is necessary to improve the strength, reduce shrinkage and increase resistance to shock. Asbestos is the customary filler and its use, coupled with the slight changes taking place during the evaporation of the solvent from the molded article and the chemical changes occurring during the baking operation, yield a finished article of rough appearance quite different from that obtained by hot pressing methods. Wood flour sometimes is added to improve the appearance but this reduces the heat resistance. China clay or other powdered mineral filler improves the appearance but diminishes the resistance to shock. Long fibred asbestos is, of course, best for strength but an article of rougher appearance is obtained than when the short fibred asbestos is used. A compromise has to be made between strength and appearance and the uses to which the molded articles are to be put governs the proportion of short and long fibred asbestos added to the mix. Talc is added to diminish the erosive effect of the composition on the molds and mica is introduced to increase the dielectric strength.

Baking.

The stoving or baking operation necessary to harden the molded pieces must be carried out very slowly to prevent blistering and deformation. A gradual heat is applied which first expels the benzol and to a greater or less degree, the heavier solvent. The size of the piece governs the time of exposure to heat, the period ranging from 12 hours for small articles to 96 hours for thick heavy pieces. The temperature range is 150-250° C. (302-482° F.). For baking purposes electrical ovens with automatic controls are useful.

Special Compositions.

The foregoing description indicates the general procedure of cold molding but the variations in the operation are so extreme that the general procedure of one plant may be quite different from that utilized in another. For example, cold molded articles are sometimes made from a mixture of asphaltum and hydraulic cement. The asphaltum is softened to a workable condition by a solvent (gasoline or benzol) and is incorporated with a mixture of Portland cement and water. Asbestos is added to improve the strength. Articles are molded from this stock, allowed to set and finally baked or immersed in a bath of hot oil to eliminate water and fill the pores with oil; thereby improving the water-resistant qualities. Plaster of Paris may be used in lieu of Portland cement. Instead of incorporating filler and binder by means of a solvent the materials may be incorporated by mixing on rolls.

The following serve as illustrations of various compositions for cold molding which are departures from the typical method previously described.¹ Cushing² makes a mixture of asbestos or other filler, Chinese wood oil varnish, stearine pitch and coal tar pitch. The object of the pitch is to prevent too rapid oxidation of the binder. A granular mass is obtained which can be molded in the cold and then baked for 24 hours at a gradually increasing temperature reaching about 400° F. (205° C.). Steinberg³ recommends a mixture of asbestos, sulphur, coal tar pitch, stearine pitch and castor oil. Benzol is used as the solvent. The composition in granular form is molded without heat at 3-5 tons per sq. in. The molded article is baked at a temperature increasing gradually to 232-250° C. (450-500° F.) over a period of 24 hours. During the baking volatile bodies are eliminated and a tough and durable insulating product results which will resist temperatures approaching those employed in baking, without softening or deformation.⁴

¹ Menningen, U. S. Pats. 1,119,441 and 1,119,442, December 1, 1914, avails of the combined effects of hot molding and baking, employing a mixture of Portland cement, sand, asbestos and an alcoholic solution of shellac.

² U. S. Pat. 1,255,139, Feb. 5, 1918.

³ U. S. Pat. 1,233,416, July 17, 1917.

⁴ For methods of cold molding employing sulphurized oils see Barringer process described in Chapter 19.

Cold Molding of Phenolic Condensation Products.

Hemming^b recommends the cold molding of phenol-formaldehyde condensation products. The binder is made from phenol and an excess of formaldehyde, employing ammonia as a catalyst. The mixture is heated under a reflux condenser and the density of the reaction product is carefully watched. When the specific gravity reaches 1.17 (or between 1.15 and 1.21) the material is sufficiently reacted to be incorporated with asbestos or other filler. The resulting mix is granular or lumpy. This material is molded under high pressure and immediately the article is shaped it is placed in an oven and baked to harden. Novotny^c employs for cold molding an acetaldehyde condensation product of phenol or cresol. The composition does not set on heating but retains thermoplastic properties.

Cold molding compositions have also been prepared by Redman, Weith and Brock^{da} from phenol and hexamethylenetetramine. A procedure employed by these investigators is to moisten wood flour or asbestos with a solution of hexamethylenetetramine in a phenolic body, cresol being recommended. Afterwards there is added a potentially reactive resin in powdered form. The mixture of filler and binder is introduced into a mold and subjected to a heavy molding pressure at room temperature. The molded article is removed from the mold and is subjected to heat treatment for a sufficient period of time to transform the binder into an infusible and insoluble product. One method is to mix 50 pounds of cresol with 13 pounds of hexa and incorporate with 600 pounds of asbestos pulp and 150 pounds of long-fibred asbestos. The mixture is prepared in a kneading machine at room temperature. 300 pounds of a fusible resin then are added (this may be made from phenol and hexa). The product is molded in the cold and is baked for 2 to 20 hours at a gradually increasing temperature ranging up to 160° or 200° C. While the ratio of binder to filler may be varied considerably, the best proportion of binder is about 30 per cent. A flame-proof article is produced from such a composition. A modification of the foregoing procedure^{db} involves mixing an initial fusible resin with hexa at a temperature of about 66° C. The hexa employed is sufficient to yield a product containing one methylene group for each phenolic group. Also it is desirable to add a slowly volatile solvent such as creosote oil (about 5 per cent calculated on the weight of the binder). Asbestos in the proportion of three times the weight of the binder is added. The product is dried by exposure to a current of warm air and after the drying step the material is ground to a coarse powder. This product is molded in the cold and is baked for a prolonged period, starting at about 38° C. and increasing the temperature gradually to approximately 230° C.

^b U. S. Pat. 1,125,906, Jan. 19, 1915.

^c U. S. Pat. 1,370,666, Mar. 8, 1921.

^{da} U. S. Pat. 1,339,134, May 4, 1920.

^{db} U. S. Pat. 1,358,394, Nov. 9, 1920.



FIG. 78.—Small Press for Cold Molding.

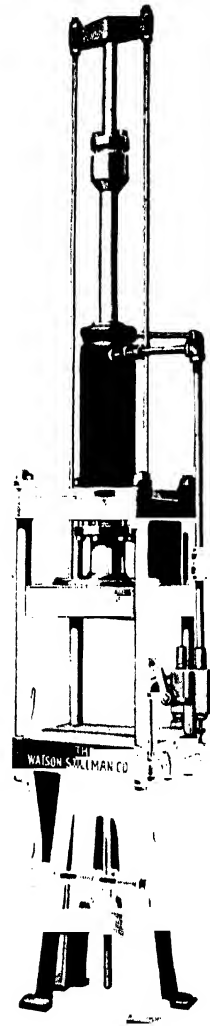


FIG. 79.—Press for Cold Molding.
(Note ejector.)

Output.

By the cold process of molding an operator commonly produces from 300 to 450 pieces per hour, using a single cavity mold. This represents an output in the neighborhood of 25 to 50 times that secured in established methods of hot molding, employing hand operated molds. With automatic presses the rate of hot molding is, of course, considerably increased. Shellac products can be hot-molded in properly designed molds somewhat more rapidly than phenol-formaldehyde condensation products. An exact comparison of output therefore is difficult and it will suffice to call attention to the far more rapid rate of molding by the cold process. The initial investment for molds thus is relatively small. Since labor cost has become so large a factor in the cost account, cold molding has developed to an industry of substantial proportions. One should, however, bear in mind that the product is not finished with the operation of molding in the cold, for the articles must thereupon be baked; whereas with hot-pressed products, the process, except for removal of fins and possibly buffing, is complete on removal of the article from the mold.

Pressing.

Usually the composition, in the form of a powder or granular material, is pressed into shape, without heat, by a series of rapid blows which are necessary to expel the confined air and shape the material in a sufficiently compact form so that it will not crumble or fall apart during removal from the mold and subsequent baking operation.

Molds.

The molds employed in the cold process, although similar to those used for hot molding, are built stronger to withstand the higher pressure and the shock to which they are subjected and do not require the highly polished surface necessary for the hot molding operation. Molds for cold molding also differ in that they must be so designed as to permit the composition, possessing little or no plasticity, to be forced into all parts of the cavity. It is occasionally necessary, therefore, to make in two or more parts, an article which by the hot molding process could be pressed in one piece. This is economically permissible because of the increased output due to the rapidity of cold molding.

Presses.

The essential feature of a press for cold molding is accurate alignment, with suitable valve equipment which makes possible a high speed of operation. The use of line pressures of from 3000 to 4000 lbs. per sq. in. has been found to be necessary in order to minimize the diameter of the press ram. A small ram is essential for the employment of high velocity pressure liquids in economical volumes.

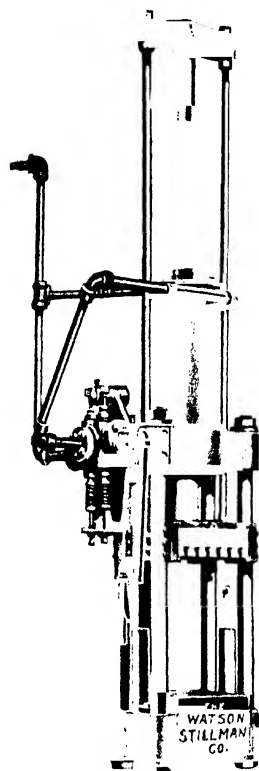


FIG. 80.—Cold Molding Press Equipped with Special Operating Valve.

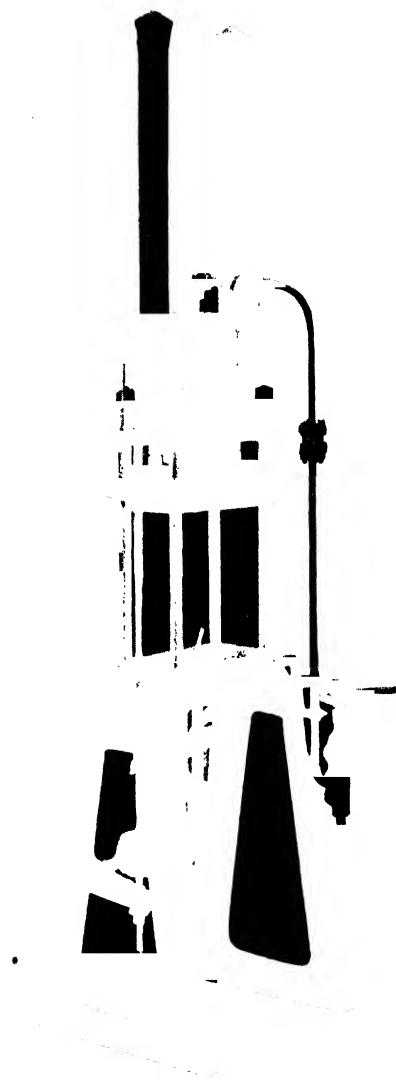


FIG. 81.—Cold Molding Press Equipped with Safety Lever.

A press of the type shown in Figs. 78 and 79 exerting 10 to 25 tons pressure per sq. in. is now employed for cold molding.⁷ The former press is equipped with a hydraulic pullback directly harnessed to the top platen. The latter is connected to the knock-out or ejector mechanism which is constructed below the lower platen. On the upward stroke of the top platen the ejector is positively actuated up to any desired position and automatically released, permitting reseating of the ejector pin in the mold preparatory to recharge of the latter. In addition to this mechanical device an auxiliary hand lever is provided for holding the ejector in the desired position when molding certain articles such as fuse plugs with a screw thread which must be unscrewed to effect removal. A three-way valve (see also Fig. 80)⁸ of sensitive control and requiring minimum effort to operate, greatly facilitates rapid molding with this press.

Fig. 81 shows a press with a safety device provided to prevent accidental closing of the press during the charging of the mold. A secondary locking lever is arranged on the left side of the press, which must be depressed with the left hand before the main operating valve can be opened. This necessitates the molder using both hands outside the line of the press and thus prevents bodily injury.

On presses above 25 tons pressure a hydraulic ejector is usually provided. Fig. 82 illustrates an ejector of this character which is operated directly by means of a secondary valve at the left of the press.

Method of Molding.

The accepted practice in the cold molding operations is to arrange the bottom of the molds with a flat working surface. At the rear, flush with the mold surface, a pan receptacle is provided to hold a supply of molding composition. The molder with his left hand simply scrapes sufficient composition from the pan to fill the mold, depresses the interlocking safety lever and by means of the sensitive valve strikes the two or three blows necessary to expel the confined air and shape the composition. Opening of the mold automatically ejects the molded piece.

Secrecy in Cold Molding.

In general, much unwarranted mystery attaches to the cold molding process. The situation is reminiscent of the ceramic industry years ago, when the potters felt that secrecy was essential to their prosperity. Of late the ceramic industry has made much progress due to an interchange of ideas through appropriate organizations and all branches of

⁷ The illustrations, Figs. 78, 81 and 82, of presses for cold molding were furnished through the courtesy of the Chas. F. Elmes Engineering Works, Chicago, Ill.

⁸ Illustrations 79 and 80 of presses for cold molding were furnished through the courtesy of the Watson-Stillman Co., New York, N. Y.

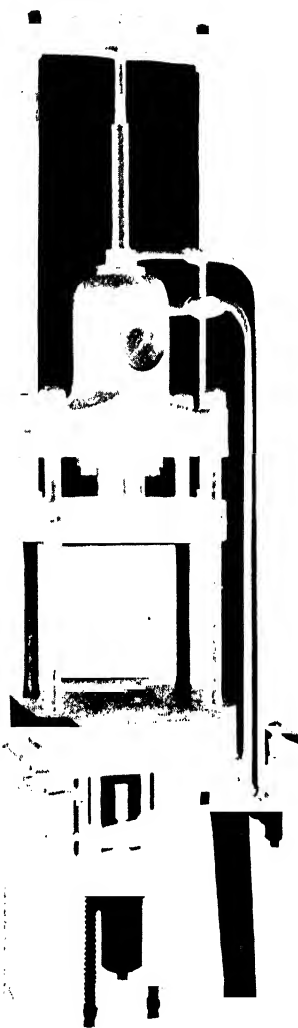


FIG. 82.—Cold Molding Press for Heavy Duty.

plastics undoubtedly would receive a desirable stimulus through similar channels. The art of molding plastics is a constantly changing one and that which is in vogue today may be obsolete tomorrow. The molding industry can greatly facilitate progress in its several fields by arriving at a greater freedom of interchange of thought and experience.

Chapter 27.

Tests of Quality of Molded Articles.

Some manufacturers and many of the consumers of molded articles have been lacking adequate data concerning the properties of the molding compositions made or used by them. Although considerable information has been obtained by manufacturers of molding compositions on the electrical insulating properties and the mechanical properties of their products, usually the data have been obtained from unrelated sources and seldom have determinations, consistent throughout, been made on the same sample of material. Naturally misunderstandings between the manufacturer, molder and consumer have arisen from time to time because of such lack of information and, all too frequently, unsuitable molding compositions have been employed with resultant dissatisfaction and loss of business. On the other hand, compositions costly in themselves and requiring a high labor cost in molding have been employed for purposes where requirements were not rigid and where the use of a composition possessing only moderately good properties, but proportionately less costly, would have served the purpose equally well. The cost of molded products is sufficiently high to warrant a careful study of the demands made upon the composition for the particular purpose in hand. A suitable specification should be prepared and submitted to manufacturers of molding compositions. Frequently a cheaper grade of material can be used than that originally contemplated. Standard tests have been prepared by both the Bureau of Standards and the American Society for Testing Materials, the methods advocated by the latter being included in this chapter. It is therefore possible to furnish numerical values, although to a limited extent, for the various properties demanded which will be applicable to molding compositions of all classes.

The Bureau of Standards has recognized the necessity for standardization of molding compositions and has made a careful study of the properties of electrical insulating materials of certain types.¹ The Bureau undoubtedly will continue this important work so that in the future entirely adequate data and tests will be at hand to make reliable comparisons on molded and laminated products, for purposes other than the requirements of the electrical field. Many of the values

¹ See Bur. of Standards Scientific Paper 234, *Insulating Properties of Solid Dielectrics*; also Technologic Paper 216, *Properties of Electrical Insulating Materials of the Laminated Phenol-Methylene Type*.

determined for electrical purposes, such, for instance, as the mechanical thermal and chemical properties, are of course useful in determining the applicability of molded material in other cases.

Radio Insulation.⁹

With the advent of radio apparatus the necessity of obtaining suitable insulation resulted in a thorough investigation by the Bureau of Standards of the properties of various insulating materials. Previously, the manufacturers of electrical insulation had furnished data on their products, which was of value for many purposes in low frequency and direct-current work but little or no literature was available on the value of the various insulating materials with high frequency (radio) currents. The Bureau of Standards, with its customary thoroughness and after considerable study, has devised methods of obtaining numerical values for the more important properties of radio insulating materials and has made many tests thereon, the results of which have been published.² The information obtained, while of undoubted value to electrical engineers, is in many cases poorly co-ordinated by the molder or chemist responsible in large measure for the present development of radio insulation. An attempt has been made, therefore, to explain, briefly, the meaning of the terms and values, so often employed by our electrical friends.

Power Loss. Phase Difference.

To one interested in the development or correct use of an insulating material to be subjected to radio-frequency voltages, the phase difference probably furnishes the best single basis for judgment of the material. When alternating current flows in a condenser having a solid insulator between the plates, the current is not exactly 90 degrees out of phase with the impressed voltage because of *power loss*. Instead of being 90 degrees the *phase angle* is a slightly smaller value. The difference between the *phase angle* and 90 degrees is the *phase difference*. The value of *phase difference* at radio frequencies largely determines the radio-frequency voltages the insulation will stand without injury. One of the principal limitations of an insulating material to be used in alternating current apparatus is measured by the magnitude of the *power loss*.

In radio insulation *power loss* introduces resistance into the circuit and diminishes selectivity. It is caused by *dielectric absorption* or *dielectric viscosity* which generates heat in the insulation when a varying current flows in it. The system of two opposite electrodes in a circuit separated by a solid *dielectric* (insulator) may be considered as a condenser. On closing the circuit, a current will flow through, and for some time be absorbed by, the dielectric. This absorption current decreases with the time but may not become negligible for several

²Data for this section obtained from Technologic Paper No. 216 and Sc. Paper No. 234, Bureau of Standards. Note forthcoming paper of Bureau of Standards on "Methods of Measuring the Properties of Electrical Insulating Materials," by J. H. Dellinger and J. L. Preston.

hours. However, when the material is used in a radio condenser the absorption is always at its peak, due to high frequency. The magnitude of the loss is best determined by measuring the *phase difference*, which varies with different insulators. *Phase difference* is closely related to the *power factor*, being, in most cases, equal to it. It is usually expressed in degrees and the product of the phase difference in degrees and 1.75 gives the power factor in per cent.

When a solid insulating material is used as a means of supporting and insulating binding posts, contacts or wires carrying alternating current, there is in reality a condenser or series of condensers between these conducting pieces with the insulating material as the dielectric.

Phase difference may be expressed as a ratio of the power dissipated in the form of heat to the total power flowing. The effect of the energy lost as heat is cumulative. The initial heating lowers the electrical resistance of the insulating material, thus causing greater current conduction and increased heating. Thus, when high voltage is used, the insulating material gradually becomes conductive and a flash-over or breakdown occurs. A knowledge of phase difference or power factor throws light on the basic theory of action of electrical insulating media.

Dielectric Constant.

This is an important property of an insulator which is to be used for a condenser. It determines the amount of alternating current which flows when an alternating voltage is impressed on a condenser. Thus, it largely determines the extent to which the condenser heats and the high-frequency voltage at which the insulator is injured. The dielectric constant of air is 1 and that of most substances is between 1 and 10, except water which has a dielectric constant of 81.

Voltage Effects.

The measurement of flash-over voltage and endurance voltage at radio frequencies is of value for determining the suitability of an insulation when high voltages are employed. Materials of this character are used to support the parts of high voltage radio frequency generators. At high frequencies the flash-over, breakdown and endurance voltage is very much lower than at low frequencies.

Flash-over voltage is the effective radio-frequency voltage necessary to arc over the surface of an insulating material between skirted brass studs, 2 cm. in diameter, placed with a distance of 2 cm. between their nearest points. (Bureau of Standards.)

Breakdown voltage is that at which the insulator heats and becomes a conductor, or permits the current to arc through it. The phenomenon depends on a number of factors, some of which are, the dielectric constant, phase difference, frequency, voltage and time of application.

Electrical Resistivities.

The current which flows between two conductors insulated from each other by a solid material is made up of two parts—(1) that which flows through the insulator proper and (2) that which flows

through a film of moisture or other semi-conducting matter *on the surface* of the insulator. The relative amounts of these depend on the relative resistances of the two paths. The resistance of the first path (1) is measured as *volume resistivity* and that of the second (2) as *surface resistivity*.

Since water, even if very pure, conducts much better than the ordinary solid insulators, a very thin film of water may give much less resistance than the insulator. Surface resistivity depends on the thickness of the film and is not a property solely of the material of the film. Surface resistivity is a property of the insulating material upon which the film is deposited. It is greatly affected by the humidity. For example, a certain insulation having a surface resistivity of 1000×10^8 ohms at a 24 per cent relative humidity, showed a resistivity of 300×10^8 at 50 per cent relative humidity.

STANDARD METHODS OF TESTING MOLDED INSULATING MATERIALS³

Material Covered.

1. These tests are intended to apply to all solid insulating materials that are formed in molds by the application of pressure, either with or without heat.

I. TENSILE STRENGTH

Apparatus.

2. Any standard testing machine may be used. Special clips (see Fig. 83 of hardened steel shall be used, hung from links held in the jaws of the machine, so that the pull is central at all times, to avoid any transverse strain.

Specimen.

3. The standard test specimen shown in Fig. 83 shall be used for the tension test. It shall be molded in a hardened and ground steel mold to the dimensions given in Fig. 83.

Method.

4. (a) Five specimens shall be tested in the condition in which they are received.

Three specimens shall be tested after heating in an oven for one hour at a temperature which is 10°C . (18°F .) below the distortion point of the material, as determined in accordance with Sections 18 to 21. Each specimen shall be taken from the oven and tested immediately while hot.

Two specimens shall be tested after they have been entirely immersed in water for 48 hours at normal room temperature. The specimens shall be pulled apart at normal room temperature of about 20°C . (68°F .) after the surface water has been removed by wiping with a dry cloth.

³ American Society of Testing Materials. Proposed as tentative, 1917; adopted in amended form, 1922.

measured by a micrometer at the center of the specimen, that is, the point of minimum section.

(c) The ultimate tensile strength in pounds per square inch or in kilograms per square centimeter of each specimen, calculated from the minimum area measured at the center of the test specimen before the load is applied.

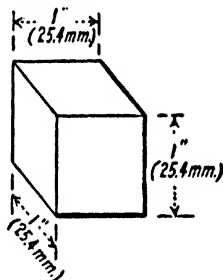
(d) The character of the material tested, with description of how it acts under stress.

(e) The speed in inches or centimeters per minute at which the jaws traveled during the test.

II. COMPRESSIVE STRENGTH

Apparatus.

6. Any standard testing machine may be used. The pressure head used for standard compressive strength tests of cement blocks is satisfactory for this purpose. A sheet of soft annealed copper about $\frac{1}{32}$ in. (1 mm.) thick, or heavy blotting paper, shall be placed above and below the specimen to equalize irregularities.



*Manufacturer's Name and *Test
Specimen No. 3 " Molded on Top
in Small Round Body Raised
Letters.
Make Steel Mold to these Dimensions.
Limits ± 0.002 (0.05 mm.)*

FIG. 84.—Compression Test Specimen
(Specimen No. 3).

Specimen.

7. The test specimen shall be molded in the form of a cube from a hardened steel mold, ground to the dimensions shown in Fig. 84.

Method.

8. (a) Five specimens shall be crushed in the condition in which they are received.

Three specimens shall be crushed after heating for one hour at a temperature which is 10° C. (18° F.) below the distortion point of the material as determined in accordance with Sections 18 to 21. Each specimen shall be taken from the oven and tested immediately while hot.

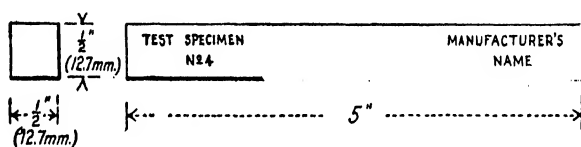
Two specimens shall be crushed after immersion in water at normal room temperature for 48 hours, with all surface water wiped off with a dry cloth.

(b) The load shall be applied in a direction at right angles to that in which the pressure was applied in molding, and at such a rate of speed that will permit the beam to be kept well balanced from zero load until the specimen is crushed. For the best results use the slowest possible speed.

Report.

9. The report of test shall include:

- (a) The dimensions of each specimen in inches or in millimeters;
- (b) The load in pounds or kilograms, on each specimen at the first sign of failure;
- (c) The ultimate compressive strength in pounds per square inch or kilograms per square centimeter, of each specimen, calculated from the measured area of each specimen before the load is applied;
- (d) The general character of the material tested, with description of how it acts under the applied load;
- (e) The speed in inches or centimeters per minute at which the jaws traveled during the test.



Make Steel Mold to these Dimensions. Limits ± 0.002 (0.05 mm.)

FIG. 85.—Transverse Test Specimen No. 4.

III. TRANSVERSE STRENGTH

Apparatus.

10. Any standard testing machine may be used. The specimen shall be supported on two steel blocks, with corners rounded to $\frac{1}{16}$ -in. (1.5-mm.) radius. These supports shall be not more than 4 in. (102 mm.) nor less than 2 in. (51 mm.) apart. The load shall be applied on top of the specimen in a direction at right angles to the direction in which the piece was molded, by means of a wedge-shaped pressure piece, the edge of which is rounded to a $\frac{1}{8}$ -in. (3-mm.) radius, extending across the specimen with the edge parallel to the edges of the two supports. The angle of the wedge shall be approximately 45 deg. and the load shall be applied at right angles to the specimen midway between the supports. The specimen shall be laid flat upon the supports at equal distances from the edge at each end.

Specimen.

11. The test specimen shall be molded from a hardened steel mold, ground to the dimensions shown in Fig. 85.

Method.

12. (a) Four specimens shall be tested in the condition in which they are received.

Three specimens shall be tested after immersion in water at normal room temperature for 48 hours with all surface water wiped off with a dry cloth.

(b) The load shall be applied at as slow a speed as possible, so that the beam may be well balanced from zero load until the first sign of failure. All tests shall be made at room temperature of about 20° C. (68° F.). Measurements of the deflection may be taken for very elastic materials.

Report.

13. The report of tests shall include:

(a) The thickness and width of each specimen as measured by a micrometer in inches or millimeters;

(b) The load on each specimen in pounds or in kilograms at the first sign of failure;

(c) The maximum fibre stress in pounds per square inch or in kilograms per square centimeter calculated from the formula:

$$S = \frac{3Pl}{2bd^2}$$

in which S = maximum fibre stress, P = load applied, l = distance between the support, b = width of specimen, and d = depth of specimen;

(d) The rate at which the load was applied;

(e) The amount of deflection at the center in inches or in millimeters;

(f) The distance between the supports in inches or in millimeters.

IV. DIELECTRIC STRENGTH

Apparatus.

14. (a) Any well-designed high tension transformer connected to an alternating current supply having as nearly a true sine wave as possible, may be used. The transformer and the source of supply of energy shall be not less than 2 kva. for voltages of 50,000 volts or less, and not less than 5 kva. for voltages above 50,000 volts. The frequency shall not exceed 100 cycles per second.

(b) Regulation shall be so controlled that the high tension testing voltage taken from the secondary of the testing transformer can be raised gradually from any point and in no case more than 500 volts at a step. The control may be made by generator field regulation, with an induction regulator, or with a variable ratio auto transformer. Any method of regulating the voltage is satisfactory which does not distort the wave more than 10 per cent from a sinusoidal shape.

(c) The voltage may be measured by any approved method which gives root-mean-square values, preferably by means of a voltmeter connected to a special voltmeter coil in the high tension winding of the testing transformer or to a separate step-down instrument potential

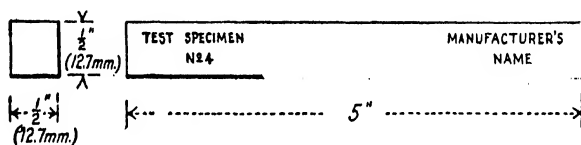
Two specimens shall be crushed after immersion in water at normal room temperature for 48 hours, with all surface water wiped off with a dry cloth.

(b) The load shall be applied in a direction at right angles to that in which the pressure was applied in molding, and at such a rate of speed that will permit the beam to be kept well balanced from zero load until the specimen is crushed. For the best results use the slowest possible speed.

Report.

9. The report of test shall include:

- (a) The dimensions of each specimen in inches or in millimeters;
- (b) The load in pounds or kilograms, on each specimen at the first sign of failure;
- (c) The ultimate compressive strength in pounds per square inch or kilograms per square centimeter, of each specimen, calculated from the measured area of each specimen before the load is applied;
- (d) The general character of the material tested, with description of how it acts under the applied load;
- (e) The speed in inches or centimeters per minute at which the jaws traveled during the test.



Make Steel Mold to these Dimensions. Limits ± 0.002 (0.05 mm.)

FIG. 85.—Transverse Test Specimen No. 4.

III. TRANSVERSE STRENGTH

Apparatus.

10. Any standard testing machine may be used. The specimen shall be supported on two steel blocks, with corners rounded to $\frac{1}{16}$ -in. (1.5-mm.) radius. These supports shall be not more than 4 in. (102 mm.) nor less than 2 in. (51 mm.) apart. The load shall be applied on top of the specimen in a direction at right angles to the direction in which the piece was molded, by means of a wedge-shaped pressure piece, the edge of which is rounded to a $\frac{1}{8}$ -in. (3-mm.) radius, extending across the specimen with the edge parallel to the edges of the two supports. The angle of the wedge shall be approximately 45 deg. and the load shall be applied at right angles to the specimen midway between the supports. The specimen shall be laid flat upon the supports at equal distances from the edge at each end.

Specimen.

11. The test specimen shall be molded from a hardened steel mold, ground to the dimensions shown in Fig. 85.

terials which resist high temperatures may be made above 125° C. (257° F.) when required.

Two specimens shall be punctured after they have had the rim immersed in melted paraffin for a depth of 1 in. (25.4 mm.) and have been entirely immersed in water for 48 hours at normal room temperature of about 20° C. (68° F.). The surface of the specimen shall be wiped off with a dry cloth to remove all trace of excessive surface moisture and the puncture test immediately made.

(c) The results from specimens where puncture takes place up on the side of the specimen instead of through the bottom shall be discarded. Experience shows that very plastic materials which flow easily in the mold always puncture through the bottom, while materials which do not mold readily will often puncture through the side walls of the specimen at some distance up from the bottom.

Report.

17. The report of test shall include:

(a) The thickness of the bottom of each specimen measured with a micrometer in the direction perpendicular to the bottom surface, and also the thickness at the point of puncture, regardless of the path taken by the discharge. The thickness of each specimen shall be given in mils or in millimeters;

(b) The puncture voltage of each test specimen expressed in terms of the effective (root-mean-square) value;

(c) The volts per mil or per millimeter as calculated from the measured thickness of the bottom of the specimen;

(d) The general character of the material tested with regard to leakage, if any is observed.

V. DISTORTION UNDER HEAT

Apparatus.

18. A special apparatus shall be used for this test as shown in Fig. 87. The specimen is supported on steel supports, 4 in. (102 mm.) apart with the load applied on top of the specimen vertically and midway between the supports, the same as for the transverse test, Section 10. The machine shall be arranged to apply to a load of 5½ lb. (2.5 kg.). The specimen shall be placed in an air bath surrounded by an oil bath which is so arranged that its temperature may be raised gradually. The machine shall be so arranged that the deflection of the specimen at its center between the supports can be measured on a scale in mils or millimeters and shall be equipped with a thermometer so that the temperature of the specimen can be recorded at any time. The machine may be arranged to automatically shut off the heat and sound an alarm as soon as the required deflection is reached.

Specimen.

19. The same test specimen shall be used for this test as required for the transverse strength test, Section 11, molded from a hard steel and mold ground to the dimensions given in Fig. 85.

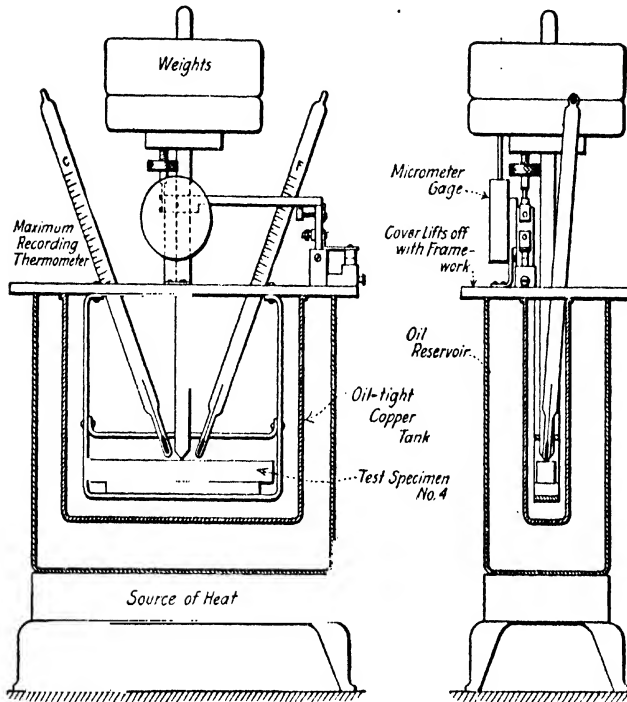


FIG. 87.—Machine for Temperature Tests.

Method.

20. Three test specimens shall be tested in the condition in which they are received, starting at normal room temperature of about 20° C. (68° F.) and increasing the temperature gradually at the rate of approximately 1° C. every two minutes.

The distortion point shall be considered the temperature at which the specimen has deflected 10 mils (0.254 mm.) at the center between the supports.

Report.

21. The report of test shall include:

- (a) The breadth and depth of each specimen measured at the center with a micrometer in inches or in millimeters;
- (b) The distortion point in degrees Centigrade or in degrees Fahrenheit;
- (c) The length of time in minutes required for each specimen to deflect 10 mils (0.254 mm.);
- (d) Any peculiar characteristics of the material as noted either during the test or after the specimen is removed from the machine;
- (e) A curve for each test specimen showing the time in minutes

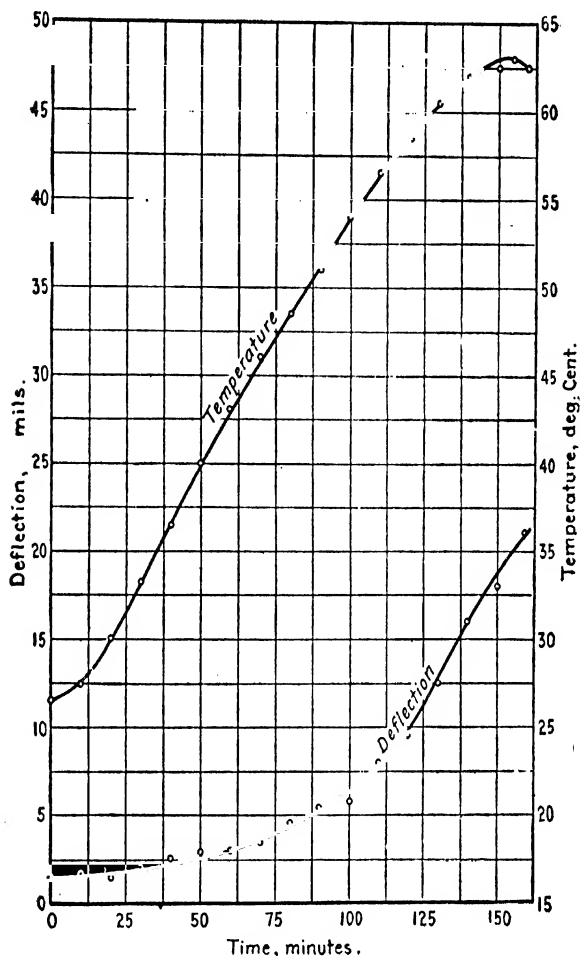


FIG. 88.—Typical Curve from Temperature Test.

horizontally and the amount of deflection and also the temperature at given intervals, as vertical ordinates as shown in Fig. 88.

VI. EFFECT OF MOISTURE

Apparatus.

22. Any good chemical balance, a beaker of water at normal room temperature of about 20° C. (68° F.), and an oven of any standard make capable of maintaining a uniform temperature of 100° C. (212° F.) with a variation allowed of $\pm 5^\circ$ C.

Specimen.

23. The test specimen No. 1 shown in Fig. 86 shall be used for this test. After the puncture tests prescribed in Section 16 (b), are completed on the five specimens, three of them shall be taken and the

entire rim of each specimen shall be sawed off with a hack saw $\frac{1}{4}$ in. (6 mm.) back from the top edge of the specimen so as to expose a more or less uniformly cut surface.

Method.

24. Weigh each of the three test specimens after the rim has been sawed off. If the material softens readily at moderate temperatures, the specimen may be placed in a desiccator for 24 hours, or in an oven at a temperature of 50° C. (122° F.), permissible variation $\pm 5^{\circ}$ C., for 24 hours. For materials which do not soften readily, the specimen shall be placed in an oven heated to 100° C. (212° F.), permissible variation $\pm 5^{\circ}$ C., for 24 hours. After drying, the pieces shall be cooled in a desiccator and weighed again at normal room temperature. The specimens shall be placed in water, wholly immersed, for 100 hours at normal room temperature. They shall then be removed from the water at the end of 100 hours, all surface water wiped off with a dry cloth, and the specimens weighed immediately.

Report.

25. The report of test shall include:

- (a) The original weight of each specimen;
- (b) The dry weight of each specimen;
- (c) The weight of each specimen after immersion for 100 hours;
- (d) The percentage of moisture contained in each test specimen as received, and the percentage of moisture absorbed during the 100 hours, taking the dry weight as 100 per cent.

All weights shall be given in grams.

Effect of Pressure Employed in Molding.

A series of tests by Schob, Mitt. Materialprüf, 1922, 40, 156; J. S. C. I. 1923, 42, 103 A, furnish information on the effect of variations of pressure employed in molding and the character of the surface of the molded article upon the mechanical properties of hot and cold molded products. The investigation included bending, torsion, and impact tests and these were carried out on samples which during manufacture had been submitted to normal pressure, or pressure 30 per cent less than, or in excess of normal pressures. The samples were used both polished and unpolished, and tests were made both at room and higher temperatures. No definite relation was found between the mechanical properties of the materials and the pressure used in manufacture. The unpolished samples were in general superior to the polished samples in mechanical properties, but the difference was usually small.

CAPACITIES OF HYDRAULIC RAMS IN TONS FOR VARIOUS DIAMETERS AND PRESSURES

PRESSURE IN POUNDS PER SQUARE INCH																								
DIA.	300	500	600	750	1000	1200	1500	1800	2000	2250	2500	2750	3000	3250	3500	4000	4500	5000	5500	6000	6500	7000	Gals. per 1" Stroke	Area
2	1.47	1.8	1.94	2.2	2.7	3.1	3.8	4.5	5.0	5.6	6.3	6.9	7.7	8.4	9.2	10.4	11.5	12.6	13.7	14.8	15.9	17.0	.013	3.14
3	1.88	2.3	2.5	2.9	3.5	4.0	4.9	5.8	6.5	7.3	8.2	9.0	10.0	11.0	12.1	13.6	15.0	16.4	17.8	19.2	20.6	22.0	.030	7.06
4	2.04	2.5	2.7	3.2	3.9	4.4	5.4	6.4	7.2	8.2	9.2	10.1	11.2	12.3	13.5	15.2	16.8	18.4	19.9	21.5	23.0	24.5	.034	12.56
5	2.25	2.8	3.0	3.6	4.3	4.9	6.0	7.1	8.0	9.1	10.2	11.2	12.3	13.5	14.8	16.8	18.6	20.4	22.1	23.8	25.5	27.1	.034	18.84
6	2.45	3.1	3.3	4.0	4.8	5.4	6.6	7.8	8.8	10.0	11.2	12.3	13.5	14.8	16.2	18.5	20.6	22.6	24.5	26.4	28.3	30.1	.034	28.27
7	2.73	3.5	3.8	4.6	5.5	6.2	7.6	9.0	10.1	11.4	12.7	14.0	15.3	16.7	18.2	21.0	23.2	25.4	27.5	29.6	31.7	33.7	.034	38.48
8	3.14	4.1	4.4	5.4	6.4	7.2	8.8	10.4	11.6	13.1	14.6	16.1	17.6	19.1	20.7	24.0	26.4	28.8	31.1	33.4	35.7	37.9	.034	50.26
9	3.55	4.7	5.0	6.1	7.2	8.1	9.9	11.6	12.9	14.6	16.3	18.0	19.7	21.4	23.1	27.0	29.6	32.2	34.7	37.2	39.7	42.1	.034	63.62
10	4.00	5.3	5.6	6.8	8.1	9.1	11.1	13.0	14.4	16.3	18.2	20.1	22.0	23.9	25.8	30.0	32.8	35.6	38.4	41.2	44.0	46.7	.034	78.54
11	4.50	6.0	6.3	7.6	9.1	10.2	12.4	14.4	15.9	18.0	20.1	22.2	24.3	26.4	28.5	33.0	36.0	39.0	42.0	45.0	48.0	51.0	.034	95.00
12	5.00	6.6	6.9	8.4	10.0	11.2	13.6	15.7	17.3	19.6	21.8	24.0	26.2	28.4	30.6	35.4	38.6	41.8	45.0	48.2	51.4	54.6	.034	113
13	5.50	7.3	7.6	9.2	11.0	12.3	14.8	17.1	18.8	21.3	23.7	26.1	28.5	30.9	33.3	38.4	41.8	45.2	48.6	52.0	55.4	58.8	.034	132
14	6.00	8.0	8.3	10.0	12.0	13.4	16.0	18.5	20.4	23.0	25.5	28.0	30.5	33.0	35.5	40.8	44.4	48.0	51.6	55.2	58.8	62.4	.034	154
15	6.50	8.7	9.0	10.8	13.0	14.5	17.2	20.0	21.9	24.6	27.3	30.0	32.7	35.4	38.1	43.6	47.4	51.2	55.0	58.8	62.6	66.4	.034	176
16	7.00	9.3	9.6	11.6	13.8	15.4	18.2	21.2	23.2	26.0	28.8	31.6	34.4	37.2	39.9	45.6	49.6	53.6	57.6	61.6	65.6	69.6	.034	201
17	7.50	10.0	10.3	12.3	14.6	16.2	19.2	22.4	24.4	27.2	30.0	32.8	35.6	38.4	41.2	47.0	51.2	55.4	59.6	63.8	68.0	72.2	.034	227
18	8.00	10.6	10.9	13.0	15.4	17.0	20.0	23.4	25.4	28.2	31.0	33.8	36.6	39.4	42.2	48.0	52.4	56.8	61.2	65.6	70.0	74.4	.034	254
19	8.50	11.2	11.5	13.6	16.0	17.6	20.6	24.0	26.0	28.8	31.6	34.4	37.2	39.9	42.6	48.4	52.8	57.2	61.6	66.0	70.4	74.8	.034	281
20	9.00	11.8	12.1	14.0	16.4	18.0	21.0	24.4	26.4	29.2	32.0	34.8	37.6	40.4	43.2	49.0	53.6	58.0	62.4	66.8	71.2	75.6	.034	314
20 1/2	9.50	12.4	12.7	14.6	17.0	18.6	21.6	25.0	27.0	29.8	32.6	35.4	38.2	41.0	43.8	49.6	54.4	58.8	63.2	67.6	72.0	76.4	.034	330
21 1/2	10.00	13.0	13.3	15.2	17.6	19.2	22.2	25.6	27.6	30.4	33.2	36.0	38.8	41.6	44.4	50.4	55.2	59.6	64.0	68.4	72.8	77.2	.034	346
22 1/2	10.50	13.6	13.9	15.6	18.0	19.6	22.6	26.0	28.0	30.8	33.6	36.4	39.2	42.0	44.8	50.8	55.6	60.0	64.4	68.8	73.2	77.6	.034	363
23 1/2	11.00	14.2	14.5	16.2	18.6	20.2	23.2	26.6	28.6	31.4	34.2	37.0	39.8	42.6	45.4	51.4	56.2	60.6	65.0	69.4	73.8	78.2	.034	380
24 1/2	11.50	14.8	15.1	16.8	19.2	20.8	23.8	27.2	29.2	32.0	34.8	37.6	40.4	43.2	46.0	52.0	56.8	61.2	65.6	70.0	74.4	78.8	.034	397
25 1/2	12.00	15.4	15.7	17.4	19.8	21.4	24.4	27.8	29.8	32.6	35.4	38.2	41.0	43.8	46.6	52.6	57.4	61.8	66.2	70.6	75.0	79.4	.034	415
26 1/2	12.50	16.0	16.3	18.0	20.4	22.0	25.0	28.4	30.4	33.2	36.0	38.8	41.6	44.4	47.2	53.2	58.0	62.4	66.8	71.2	75.6	80.0	.034	432
27 1/2	13.00	16.6	16.9	18.6	21.0	22.6	25.6	29.0	31.0	33.8	36.6	39.4	42.2	45.0	47.8	53.8	58.6	63.0	67.4	71.8	76.2	80.6	.034	450
28 1/2	13.50	17.2	17.5	19.2	21.6	23.2	26.2	29.6	31.6	34.4	37.2	40.0	42.8	45.6	48.4	54.4	59.2	63.6	68.0	72.4	76.8	81.2	.034	468
29 1/2	14.00	17.8	18.1	19.8	22.2	23.8	26.8	30.2	32.2	35.0	37.8	40.6	43.4	46.2	49.0	55.0	59.8	64.2	68.6	73.0	77.4	81.8	.034	486
30 1/2	14.50	18.4	18.7	20.2	22.8	24.4	27.4	30.8	32.8	35.6	38.4	41.2	44.0	46.8	49.6	55.6	60.4	64.8	69.2	73.6	78.0	82.4	.034	504
31 1/2	15.00	19.0	19.3	20.6	23.2	24.8	27.8	31.2	33.2	36.0	38.8	41.6	44.4	47.2	50.0	56.0	60.8	65.2	69.6	74.0	78.4	82.8	.034	522
32 1/2	15.50	19.6	19.9	21.2	23.8	25.4	28.4	31.8	33.8	36.6	39.4	42.2	45.0	47.8	50.6	56.6	61.4	65.8	70.2	74.6	79.0	83.4	.034	540
33 1/2	16.00	20.2	20.5	21.8	24.4	26.0	29.0	32.4	34.4	37.2	40.0	42.8	45.6	48.4	51.2	57.2	62.0	66.4	70.8	75.2	79.6	84.0	.034	558
34 1/2	16.50	20.8	21.1	22.2	24.8	26.4	29.4	33.0	35.0	37.8	40.6	43.4	46.2	49.0	51.8	57.8	62.6	67.0	71.4	75.8	80.2	84.6	.034	576
35 1/2	17.00	21.4	21.7	22.8	25.4	27.0	30.0	33.6	35.6	38.4	41.2	44.0	46.8	49.6	52.4	58.4	63.2	67.6	72.0	76.4	80.8	85.2	.034	594
36 1/2	17.50	22.0	22.3	23.4	26.0	27.6	30.6	34.2	36.2	39.0	41.8	44.6	47.4	50.2	53.0	59.0	63.8	68.2	72.6	77.0	81.4	85.8	.034	612
37 1/2	18.00	22.6	22.9	24.0	26.6	28.2	31.2	34.8	36.8	39.6	42.4	45.2	48.0	50.8	53.6	59.6	64.4	68.8	73.2	77.6	82.0	86.4	.034	630
38 1/2	18.50	23.2	23.5	24.6	27.2	28.8	31.8	35.4	37.4	40.2	43.0	45.8	48.6	51.4	54.2	60.2	65.0	69.4	73.8	78.2	82.6	87.0	.034	648
39 1/2	19.00	23.8	24.1	25.0	27.8	29.4	32.4	36.0	38.0	40.8	43.6	46.4	49.2	52.0	54.8	60.8	65.6	70.0	74.4	78.8	83.2	87.6	.034	666
40 1/2	19.50	24.4	24.7	25.6	28.4	30.0	33.0	36.6	38.6	41.4	44.2	47.0	49.8	52.6	55.4	61.4	66.2	70.6	75.0	79.4	83.8	88.2	.034	684
41 1/2	20.00	25.0	25.3	26.2	29.0	30.6	33.6	37.2	39.2	42.0	44.8	47.6	50.4	53.2	56.0	62.0	66.8	71.2	75.6	80.0	84.4	88.8	.034	702
42 1/2	20.50	25.6	25.9	26.8	29.6	31.2	34.2	37.8	39.8	42.6	45.4	48.2	51.0	53.8	56.6	62.6	67.4	71.8	76.2	80.6	85.0	89.4	.034	720
43 1/2	21.00	26.2	26.5	27.4	30.2	31.8	34.8	38.4	40.4	43.2	46.0	48.8	51.6	54.4	57.2	63.2	68.0	72.4	76.8	81.2	85.6	90.0	.034	738
44 1/2	21.50	26.8	27.1	28.0	30.8	32.4	35.4	39.0	41.0	43.8	46.6	49.4	52.2	55.0	57.8	63.8	68.6	73.0	77.4	81.8	86.2	90.6	.034	756
45 1/2	22.00	27.4	27.7	28.6	31.4	33.0	36.0	39.6	41.6	44.4	47.2	50.0	52.8	55.6	58.4	64.4	69.2	73.6	78.0	82.4	86.8	91.2	.034	774
46 1/2	22.50	28.0	28.3	29.2	32.0	33.6	36.6	40.2	42.2	45.0	47.8	50.6	53.4	56.2	59.0	65.0	69.8	74.2	78.6	83.0	87.4	91.8	.034	792
47 1/2	23.00	28.6	28.9	29.8	32.6	34.2	37.2	40.8	42.8	45.6	48.4	51.2	54.0	56.8	59.6	65.6	70.4	74.8	79.2	83.6	88.0	92.4	.034	810
48 1/2	23.50	29.2	29.5	30.2	33.2	34.8	37.8	41.4	43.4	46.2	49.0	51.8	54.6	57.4	60.2	66.2	71.0	75.4	79.8	84.2	88.6	93.0	.034	828
49 1/2	24.00	29.8	30.1	30.8	33.8	35.4	38.4	42.0	44.0	46.8	49.6	52.4	55.2	58.0	60.8	66.8	71.6	76.0	80.4	84.8	89.2	93.6	.034	846
50 1/2	24.50	30.4	30.7	31.4	34.4	36.0	39.0	42.6	44.6	47.4	50.2	53.0	55.8	58.6	61.49									

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